THE PROCEEDINGS OF
THE PHYSICAL SOCIETY

VOL. 50, PART 1 *January* 1, 1938 NO. 277

THE ELECTRIC CHARGES ON SINGLE RAINDROPS AND SNOWFLAKES

BY J. ALAN CHALMERS, M.A., PH.D. (Cantab.),
Lecturer in Physics in the University of Durham (Durham Division)
AND
F. PASQUILL, B.SC.
Pemberton Research Fellow, University College, Durham

Communicated by Dr Bruce Chalmers, 10 *July* 1937. *Read* 8 *October,* 1937

ABSTRACT. An account is given of 16 months' observations on the charges of individual raindrops and snowflakes. The results show an excess of positively charged drops and of total positive charge, except for storm rain. The average charge per drop is greater in the case of negative than of positive raindrops, but the reverse holds for snowflakes. Observations were also made of the sequences of drops of one sign, of the relative proportions of drops of the two signs in different parts of a single rainfall and of the distribution in magnitude of the charges. A brief discussion is given of the problems of the origin of the charges on rain.

---

§ 1. INTRODUCTION

OBSERVATIONS of the charges carried by raindrops and other forms of atmospheric precipitation can contribute to the discussion of two of the main problems of atmospheric electricity, namely, the problem of the maintenance of the negative charge on the earth's surface in fine weather, and the problem of the origins of the electrical phenomena of stormy conditions.

The total vertical current due to precipitation must play a part in what Wormell(24) has termed the "electrical balance sheet" of the earth. If the precipitation current brings down to the earth a positive charge, then this must be added to the effect of the fine-weather current and both must be balanced by some other process or processes; on the other hand, if a negative charge is brought down, it will help to neutralize the fine-weather current. It must be pointed out that any secondary effects occurring during the rainfall should be included in the vertical current; for example, if splashing causes a separation of charge and some of this is carried upwards and does not reach the earth, then there will be a resultant vertical current differing from that carried by the actual raindrops; in the same way the ionic conduction current should be included in the total vertical current in bad weather conditions, particularly as this might have a greater value than in fine weather, owing to extra sources of ionization.

It is possible that measurements of the charges on raindrops can give some information as to the processes giving rise to electrical effects in clouds, for it seems generally agreed that water-drops must be the agency by which the charges in storm clouds are built up. In this connexion, it is clearly more useful to measure the charges on individual drops than to obtain merely the average for a large number of drops.

The majority of the measurements of the charges on rain have taken the form of a compromise between the two types of measurement discussed above. In the experiments of Elster and Geitel(8), Gerdien(9), Kähler(13), Simpson(21). Benndorf(5), Baldit(1, 2, 3), McClelland and Nolan(17, 18), Berndt(6), Schindelhauer(19), McClelland and Gilmour(16), Miss Marwick(15) and Banerji(4), a receiver was used which was shielded to prevent rain splashing into it from outside, and to avoid any effects due to field-changes; care was also taken to prevent effects due to splashing inside the receiver. In all these experiments, measurements were made of the charge brought down by the number of drops arriving on a definite area in a certain time; or, in some cases, by the number of drops in a given volume of rain. Yet most of the observers have discussed their results in connexion with the total vertical current during the precipitation, neglecting the ionic current and any secondary processes such as splashing effects.

Weiss(22) used a wire brush to receive the drops, but it was found that there were effects due to point discharges and the method was of little value. Kohlrausch(14) shielded the brush from the earth's field, and thus his observations come into the same category as those considered above.

Herath(12) has used a large area of cloth, completely exposed, as a receiver, and hence some, at least, of the secondary processes can come into operation. Schonland(20) also made some observations with a completely exposed test plate.

Gschwend(10) alone has made observations on the charges carried by individual drops, and it is clear that it is only such observations that can give accurate information about the drops. In the usual method of measurement, all that can be obtained is the average for a large number of drops, and it is not even possible to tell whether or not the charges on the drops are all of the same sign. Gschwend has discussed the fact that the average current for a number of drops is much smaller than the instantaneous current, and the same applies to the average and single charges.

Furthermore, previous observers, who have shielded their receivers, have thereby excluded any rain falling at a considerable angle to the vertical; in most cases, rain falling more obliquely than at 40° to the vertical cannot possibly be recorded. Thus, in driving rain, no observations have been possible, and consequently a fair sample of rain has not been obtained.

Most of the observers have made, in addition, simultaneous observations of other relevant quantities, e.g. potential-gradient, rate of rainfall and size of drops, but few relations have been found between these quantities and the charges on the rain.

Since the different observers referred to above have found results which show marked divergences, it was considered desirable to carry out further observations by the method of Gschwend(10), in order to obtain further information about the charges on individual drops. In view of Gschwend's result that there is no definite relation between the size and charge of a drop, it was decided to concentrate on the measurement of the charges of as many as possible of the drops falling on one particular area. To avoid missing the driving rain, the apparatus was arranged to receive as much as possible of the rain, no matter at what angle it was travelling.

§ 2. THE APPARATUS

The vessel used for the reception of raindrops is of metal and of the shape shown in figure 1. It has a height of 16 cm., a maximum diameter of 7·3 cm., and an orifice 4 cm. in diameter. It is insulated on sulphur, which is kept warm and dry by means of a heating coil. The receiver and insulator are contained in a metal vessel 16 cm. in diameter and 20 cm. high with a lid of the shape shown in figure 1; the frustum-shaped portion of the lid fits closely over the correspondingly shaped top of the receiver. This outer container and lid are connected to earth, and so the receiver is protected almost completely from variations in the earth's field. The effective aperture of the receiver is reduced by the lid to a diameter of 2·9 cm. or an area of 6·6 cm.^{2}, and the shape and dimensions of the apparatus show that drops at an angle as great as 70° to the vertical can enter the receiver.

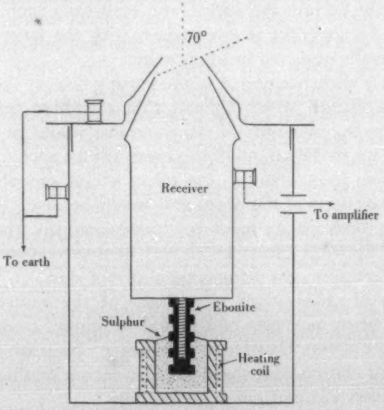


Figure 1.

The arrangement is set up on the flat roof of the Science Laboratories at Durham as far away as possible from any elevated objects. From the receiver, a shielded cable passes through a hole in the roof into the room below which contains the measuring-instrument. The latter, described in detail elsewhere by Chalmers and Pasquill$^{(7)}$, consists of a two-stage valve bridge amplifier used in conjunction with a dead-beat mirror galvanometer, and has a limit of accuracy of the order of 10^{-4} e.s.u. of charge.

Owing to the comparatively low resistance of the amplifier, there are no serious insulation difficulties. The two principal possibilities of error are concerned with effects of splashing and of sudden changes in the vertical electric field of the atmosphere. With regard to splashing, there are two aspects to be considered; the first is the possibility of the splashing out of drops entering the receiver, and the second the possibility of splashing in from outside. The first possibility is minimized by the shape of the receiver and an experimental test was performed; drops carrying a definite charge were allowed to fall from different heights, and it was found that no alteration occurred in the readings obtained even when splashing did take place in the receiver; thus the assumption that there would be no splashing out was verified. The second possibility was considered by observing the apparatus during rainfall; it was found that only in the very heaviest of rain did drops splash from the flat portion of the lid into the orifice, and even then such occasions were rare and the effect can be neglected in comparison with the large number of heavily charged drops generally observed in heavy rain.

As the receiver is slightly exposed to the earth's field at the orifice, an experimental test was performed which showed that a sudden field-change of about 6000 v. per metre in the proximity of the apparatus would be accompanied by an apparent charge of 2×10^{-3} e.s.u. on the receiver. Since such a field-change would only occur in a close thunderstorm, the effect would probably be negligible in comparison with the effects of the drops and would be much less frequent. Since the charges on the raindrops are measured instantaneously, there is no possibility of error due to any electrical effects which may be due to evaporation of the drops (cf. Gunn$^{(11)}$), the latter process being comparatively slow.

In practice, visual observations were made of the galvanometer deflections and, consequently, often only part of a period of rainfall could be examined. In particular, it was not always possible to commence observations at the beginning of the rain. During observation, the deflection corresponding to each drop was noted and a calibration was performed periodically.

Occasionally, abnormally large deflections were observed, and these could be recognized as abnormal in character, since they did not give the usual clear kick; a rough experimental test showed that these deflections were due to drops accidentally short-circuiting the space between the receiver and the lid above it; they were therefore neglected.

In very fine rain it was not found possible to make observations, probably owing to the sensitivity of the amplifier being insufficient to measure the very small charges concerned.

§ 3. EXPERIMENTAL RESULTS

From the observations performed, it has been found possible to obtain a number of general results for the whole year 1936 and the first four months of 1937, and for a seasonal variation during the period. These points have been dealt with first in the following presentation of the experimental results.

Table 1. Seasonal variation

Season	Total positive (e.s.u.)	Total negative (e.s.u.)	Ratio +ve/−ve	Surplus	Duration (min.)	Mean current (10^{-15} amp./cm^2)
*Winter, 1936	6·81	3·36	2·03	+3·45	1478	+1·9
Spring	10·82	8·65	1·25	+2·17	977	+1·8
Summer	3·63	5·54	0·65	−1·91	612	−2·6
Autumn	3·07	2·18	1·41	+0·89	493	+1·5
*Winter, 1937	8·73	5·79	1·51	+2·94	676	+3·6

* "Winter" is taken as the three months January, February and March, with the other seasons to correspond.

For the convenience of a more detailed analysis, the precipitations observed have been divided into the following groups: (i) continuous fine rain, (ii) continuous heavy rain, (iii) continuous driving rain, (iv) showers, (v) squall rain, (vi) storm rain, (vii) snow, (viii) sleet, and (ix) hail. No actual thunderstorms occurred during the observations, but "storm rain" designates rain during which the conditions approached those generally associated with thunderstorms.

To avoid confusion in terms, the word *rainfall* is adopted to signify any period of rain, of any type, during which or during part of which observations were performed. Often it was not possible to make observations continuously throughout the whole period of a rainfall, but the different periods of observation have been combined to give results for the whole rainfall.

For each separate rainfall the following data were obtained: (1) The duration of the observations, (2) the total number of drops of each sign, (3) the total charge of each sign, (4) the number of changes of sign during the rainfall, (5) the *course* of the rainfall (i.e. whether or not one sign predominated in any one part of the rainfall), and (6) the distribution in magnitude of the charges on the individual drops received during the rainfall.

From the first four sets of data the following results are obtained, and the values of these for each type of precipitation are tabulated in table 2: (*a*) the mean current per cm^2, (*b*) the ratio of total positive to total negative charge, (*c*) the number of positively and negatively charged drops, (*d*) the average positive and negative charge per drop, (*e*) the average number of sign-changes per minute, (*f*) the average sequence of positive and of negative drops.

The first two of these groups of results have been obtained by other workers by means of the more usual type of observations and here are not considered of paramount importance; they are inserted merely for the purpose of comparison with earlier results.

In table 3 the different rainfalls have been classified according to their courses and the sequences of positive and negative charges. In figure 2 the course of one example of a rainfall is considered in detail.

Table 2. Summary of results for all types of precipitation

	Continuous fine rain	Continuous heavy rain	Continuous driving rain	Showers	Squall rain	Storm rain	All types of rain	Snow	Sleet	Hail	Snow, etc.
No. of + ve rainfalls	13	14	5	5	6	2	45	5	5	3	13
No. of − ve rainfalls	5	2	0	5	1	6	19	8	1	1	10
Mean current $(10^{-15}$ amp./cm.$^2)$	+ 0·9	+ 2·5	+ 0·9	+ 0·6	+ 2·2	− 13·6	+ 1·0	+ 5·0	+ 1·5	+ 2·0	+ 3·2
$\frac{\text{Total} + \text{ve charge}}{\text{Total} - \text{ve charge}}$	2·82	1·38	1·28	1·42	9·85	0·35	1·23	1·43	1·38	1·65	1·42
No. of + ve drops	1718	4828	1296	768	201	312	9123	883	921	167	1971
No. of − ve drops	489	2806	611	523	12	355	4796	1138	452	102	1692
Average + ve charge per drop $(10^{-3}$ e.s.u.)	0·9	3·0	1·8	1·1	1·3	3·7	2·3	10·5	3·2	2·6	6·4
Average − ve charge per drop $(10^{-3}$ e.s.u.)	1·1	3·7	3·0	1·2	2·3	9·2	3·5	5·7	4·7	2·6	5·3
Average no. of sign-changes per min.	0·6	1·8	1·3	1·4	0·1	1·6	1·3	1·1	0·8	1·0	1·0
Average + ve sequence	7	4	4	3	37	3	4	4	5	4	4
Average − ve sequence	2	2	2	2	2	4	2	5	2	3	4

Table 3. Classification of rainfalls according to courses and sequences

	Continuous fine rain	Continuous heavy rain	Continuous driving rain	Showers	Squall rain	Storm rain	All types of rain	Snow	Sleet	Ha
Entirely + ve	3	0	0	1	5	0	9	0	1	1
+ ve sequences and − ve singles	9	4	3	4	1	2	23	0	0	0
+ ve sequences early − ve sequences later	2	5	0	1	0	1	9	1	0	0
Sequences of both signs	2	4	2	2	0	2	12	6	3	2
− ve sequences early + ve sequences later	0	3	0	1	0	0	4	3	1	1
− ve sequences and + ve singles	2	0	0	1	1	2	6	0	1	0
Entirely − ve	0	0	0	0	0	1	1	3	0	0

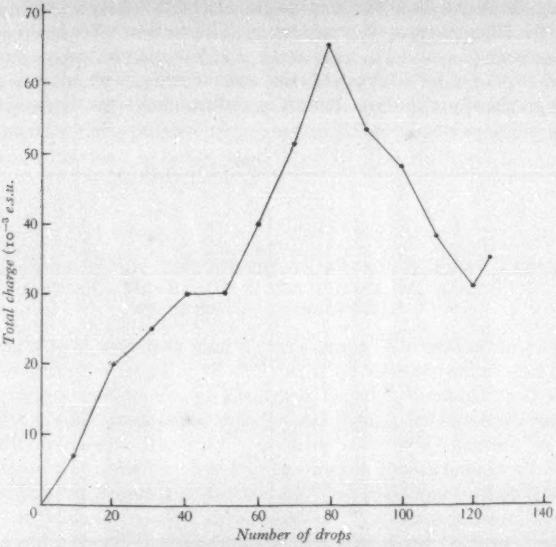


Figure 2. Example of a rainfall with positive sequences early and negative sequences later. For convenience the rainfall is divided into groups of 10 drops each. This rainfall was observed on 22 June, lasted about 40 min., and is classified as a shower.

Table 4. Distribution in magnitude of charges

Charges (10^{-3} e.s.u.)	Continuous fine rain	Continuous heavy rain	Continuous driving rain	Showers	Squall rain	Storm rain	All types of rain	Snow	Sleet	Hail	Snow, sleet and hail
> +5¼	41	662	88	18	10	72	891	319	80	23	424
+4¾ to +5¼	10	102	26	1	0	10	149	15	8	1	24
+4¼ to +4¾	3	66	8	4	1	16	98	16	5	6	27
+3¾ to +4¼	6	145	14	3	2	15	185	21	12	6	39
+3¼ to +3¾	15	149	31	10	7	8	220	38	19	6	63
+2¾ to +3¼	22	240	36	19	5	13	335	43	15	3	61
+2¼ to +2¾	19	311	58	28	7	13	436	38	25	12	75
+1¾ to +2¼	50	409	64	49	6	32	610	59	47	10	116
+1¼ to +1¾	112	561	94	66	24	28	885	73	113	20	206
+ ¾ to +1¼	250	944	212	135	37	58	1636	102	148	32	282
+ ¼ to + ¾	839	1150	515	305	79	42	2930	136	423	40	599
− ¼ to + ¼	443	138	207	204	23	6	1021	42	56	10	108
− ¾ to − ¼	261	545	170	270	2	12	1260	211	164	24	399
−1¼ to − ¾	58	523	90	74	1	32	778	215	60	13	288
−1¾ to −1¼	25	394	60	35	5	15	534	99	48	6	153
−2¼ to −1¾	18	209	25	13	2	19	286	73	33	9	115
−2¾ to −2¼	3	195	39	9	0	32	278	67	13	15	95
−3¼ to −2¾	4	117	25	6	0	24	176	43	7	8	58
−3¾ to −3¼	1	99	26	3	0	6	135	34	15	6	55
−4¼ to −3¾	3	67	8	5	0	36	119	28	8	5	41
−4¾ to −4¼	4	56	5	3	1	17	86	27	9	0	36
−5¼ to −4¾	2	74	12	4	0	13	105	14	5	1	20
< −5¼	18	478	94	27	1	148	766	308	60	13	381

Table 4 shows the distribution in magnitude of the charges on the individual drops for the different types of precipitation. The total number of drops carrying average charges 0 ($-\frac{1}{4}$ to $+\frac{1}{4}$), $\pm\frac{1}{2}$ ($\frac{1}{4}$ to $\frac{3}{4}$), ± 1 ($\frac{3}{4}$ to $1\frac{1}{4}$), etc., up to ± 5 ($4\frac{3}{4}$ to $5\frac{1}{4}$) in units of 10^{-3} e.s.u. for all types of rain, and for snow, sleet and hail combined, are shown graphically in figure 3. It must be realized that, since the finest rain is not observed and the limit of measurement is usually about 2×10^{-4} e.s.u., a large number of drops carrying charges from $-\frac{1}{4}$ to $+\frac{1}{4}\times 10^{-3}$ e.s.u. will have been missed, and consequently the centre portion of the curve can only be estimated.

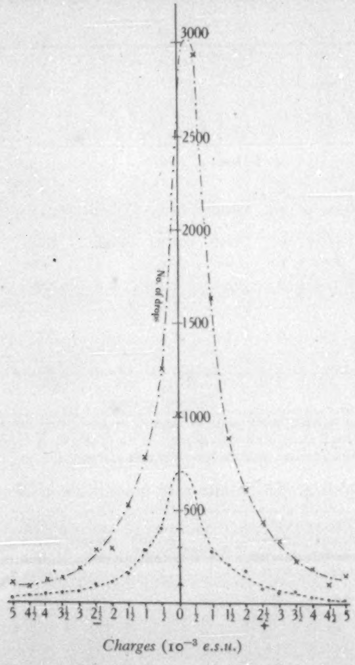


Figure 3. Distribution in magnitude of charges.
—·—·— all types of rain ------- snow, sleet and hail

Table 5. General results for the period

Total number of positively charged drops observed ...	11,094
Total number of negatively charged drops observed ...	6,488
Ratio of numbers of positive and negative drops	1·71
Total positive charge received (e.s.u.)	33·2
Total negative charge received (e.s.u.)	25·6
Ratio of total positive to total negative charge	1·30
Surplus of charge (e.s.u.)	7·6

With regard to seasonal variation, only one rainfall was observed in each April and none in August. Of the remaining months, only July showed a definite predominance of negative charge (with a mean current of $-4\cdot0\times10^{-15}$ amp./cm.^{2}), November was slightly negative, while March 1936 and September were almost neutral, despite the large number of drops observed in the latter month. All other months showed a definite positive predominance. Table 1 was obtained by grouping the months into seasons.

§4. DISCUSSION OF THE GENERAL EXPERIMENTAL RESULTS AND COMPARISON WITH THOSE OBTAINED BY PREVIOUS OBSERVERS

(*a*) *Ratio of total positive to total negative charge.* The ratio of total positive to total negative charge is found to be 1·30, or, if we leave out snow, sleet and hail, 1·23. All previous workers except Elster and Geitel(8), Gerdien(9) and Banerji(4) have found a positive-to-negative ratio greater than 1, but in actual magnitudes there is little agreement. Banerji(4), observing only thunderstorms, at Bombay found a ratio of 0·85, Baldit(1, 2, 3) at Puy-en-Velay in France found 1·36, Schindelhauer(19) at Potsdam found 1·4, Gschwend(10) at Freidberg in Switzerland 1·5, Simpson(21) at Simla in India 3·2, Miss Marwick(15) at Otago in New Zealand 3·2, McClelland and Nolan(17, 18) at Dublin 4·8, McClelland and Gilmour(16) at Dublin 5·2, Herath(12) at Kiel 15, and Schonland(20) in a few thunderstorms, in South Africa, 30.

Since the present observations have not included the finest rain, which McClelland and Nolan(17, 18) and McClelland and Gilmour(16) found to be negative and Gschwend(10) positive, the low value found for the ratio might be accounted for by accepting Gschwend's result. The divergence is still less surprising when one considers not only the effects of different climates, different predominating kinds of rain, different local conditions, different angles of reception, and different apertures, but also the method by which the ratio is obtained. In all cases except those of Gschwend and the present authors, the resultant charge only, either positive or negative, has been recorded for each definite interval or each definite volume of rain; consequently, an interval during which both positive and negative charges fall, with a predominance of positive, will be observed as positive only and will contribute only to the positive total. If, for example, the negative charges occur only for short intervals or only on small areas at once, then the observed positive-to-negative ratio would be increased by an increase of the time interval considered or of the area of the receiver. But in the present measurements and those of Gschwend, each drop is considered separately, and thus the ratio of positive to negative is less than if obtained from the other type of measurement. In illustration of this point, each rainfall can be considered as a whole, and the positive and negative surpluses can be added; this method gives a positive-to-negative ratio of 2·6.

(*b*) *Mean currents per cm*.^{2} The observations of Gerdien(9), Kähler(13) and Schindelhauer(19) give the values shown in table 6.

Table 6. Average values of vertical currents (amp./cm.^{2})

Ordinary rain	...	10^{-15}
Squall rain	...	10^{-13}
Thunder rain	...	10^{-14} to 10^{-12}

Whereas Gerdien found the current to be negative in each case, most of the later workers have found positive currents for ordinary rain and thunder rain, Simpson(21), in particular, finding large positive currents for thunder rain, while Schindelhauer(19) and Baldit(1, 2, 3) frequently observed strong negative currents for squall rain.

The present observations gave a vertical current of the order of 10^{-15} amp./cm.^{2} for fine, heavy and driving rain and showers, and in the case of the heaviest rain the current has risen to 10^{-14} amp./cm.^{2} on occasions. Squall rain gave a positive current of small magnitude, in contrast to the large negative currents observed by Schindelhauer and Baldit. On the other hand, storm rain gave a negative current of the order of 10^{-14} amp./cm.^{2}, in contrast to the large positive currents observed by Simpson(21) and Schonland(20), but in general agreement with the negative surplus found for thunder rain by Banerji(4). No currents have been observed to compare in magnitude with those previously observed, but this may be due to the absence of any very heavy rain.

(*c*) *Seasonal variation.* The present observations show a very marked seasonal variation, due principally to the negative charges on storm rain; the positive-to-negative ratio has a maximum value in winter and a minimum in summer. Schindelhauer(19) found a maximum in winter and a minimum in spring, while McClelland and Nolan(17, 18), in a series of observations from October 1911 to May 1912, found the ratio to be greatest in spring. McClelland and Gilmour(16) also found a negative excess in July, but a positive excess in August.

(*d*) *The positive-to-negative ratio for different types of precipitation.* The main points of interest lie in the very high ratio for squall rain and the very low ratio for storm rain. These are of special importance since Schindelhauer(19) found a ratio less than unity for squall rain, Gschwend(10) found 0·55, and Baldit's(1, 2, 3) ratio was only 1·1. For storm rain in India, Simpson(21) found a very high ratio (as did Schonland(20) in South Africa), but Banerji(4) found a ratio of only 0·85; under conditions nearer to those of the present observations, McClelland and Gilmour(16) found a ratio just over unity and Gschwend(10) found 1·51. Such a wide variation can be attributed only to the differences in meteorological conditions.

Previous observers have disagreed as to the electrical charges on snow. Weiss(22), Simpson(21), Gschwend(10) and Miss Marwick(15) found a positive excess, whereas Elster and Geitel(8), Kähler(13), Schindelhauer(19), McClelland and Nolan(17, 18) and McClelland and Gilmour(16) found a negative excess.

In the present observations, it was found that those snowfalls which consisted of large flakes were predominantly positive and those which consisted of small flakes were predominantly negative; this is in agreement with the results obtained by McClelland and Nolan and by Gschwend. It is probable that the divergences quoted above may be ascribed to excesses of either type of flake.

Sleet and hail (most of the latter being in the form of soft hail) both give positive and negative ratios greater than unity, which is in agreement with all previous observers with the exception of Schindelhauer.

§5. DISCUSSION OF RESULTS PECULIAR TO THE PRESENT TYPE OF OBSERVATIONS

(*a*) *The individual drops*. The results can be compared with those of Gschwend(10). The relative number of positive and negative drops is 1·71, as compared with Gschwend's value of 1·78 obtained mainly from observations of single drops at intervals. In the present work all types of precipitation, with the exception of storm rain and snow, show an excess of positive drops. In storm rain there is a slight excess of negative drops, while for snow there is a definite excess. Gschwend found an excess of positive drops in all types of precipitation except thunder rain, and in this he found approximately equal numbers of drops of both signs. However, his ratio of positive-to-negative drops for squall rain is less than in the present observations.

The mean charges per drop can be compared directly with those obtained by Gschwend. The values for all the different types of precipitation are given in table 2, but, for comparison with Gschwend, fine, heavy and driving rain and showers have been grouped together as "ordinary rain" in table 7. Since the finest rain has not been measured in the present work, agreement with Gschwend cannot be expected for ordinary rain.

Table 7. Mean charges per drop (10^{-3} e.s.u.)

	Gschwend		Present work	
	+ve	−ve	+ve	−ve
Ordinary rain	0·24	0·53	2·2	3·0
Squall rain	1·75	5·43	1·3	2·3
Thunder or storm rain	8·11	5·88	3·7	9·2
Continuous snow	0·09	0·06	10·5	5·7
Bursts of snow	5·64	4·78		

The most striking characteristic of the present observations is that for every type of rain the average negative charge per drop is greater than the average positive charge per drop. This agrees with the observations on ordinary and squall rain observed by Gschwend, but not with those on storm rain, possibly owing to the fact that no observations were made during actual thunderstorms. The present work agrees with that of Gschwend in finding approximately equal numbers of positive and negative drops during storm rain, but Gschwend obtained a positive excess due to the greater mean charge per drop on positive drops, while the reverse holds in the present observations. The greatest charges obtained were during a snowfall and reached up to $+150 \times 10^{-3}$ e.s.u. and -110×10^{-3} e.s.u. No raindrops were observed with charges greater than $\pm 90 \times 10^{-3}$ e.s.u.

For snow the results correspond except in that much of the snow observed might be considered more correctly as "continuous" rather than as "bursts".

(*b*) *Sign-changes and sequences.* Gschwend states that the most striking point emerging from continuous observations of the individual drops falling on a small area is the frequency of the changes of sign of the charges carried by the drops. He found that it was only in ordinary rain (*Landregen*) that drops carrying charges of one sign only fell on a surface of 12 cm^2 in 1 min. For fine rain he found 3 or 4 sign-changes per minute to occur frequently, while as many as 8 changes in half a minute were observed. In one thunderstorm, 60 drops fell in 3 min. and there were 38 sign-changes.

Although the reception area employed here was much less than (just over one half of) that used by Gschwend in the above cases, a comparison is possible. An analysis of the present observations shows that for all types of rain the average number of sign-changes per minute is slightly greater than unity. This appears small in comparison with Gschwend's values, but it is only an average, which is often exceeded. For example, in one storm shower lasting 9 min. there were 38 sign-changes, an average of 4 per minute; also in one rainfall of continuous heavy rain, the average number of sign-changes per minute was found to be 3; yet in parts of the rainfall there were whole minutes without any changes of sign, whereas in other parts as many as 12 sign-changes per minute were observed.

Bound up with this question of sign-changes is the question of sequences of one sign. There is one definite conclusion arising out of the observations, namely, that the sequences are more frequent than would be expected on pure chance. In some rainfalls, predominantly positive, the few negative drops are not, as might be expected, distributed at random among the positive drops, but there is a definite tendency for the negative drops to occur at nearly the same time, giving a negative sequence. This must be interpreted to mean, in the first place, that there is a process (or processes) for giving raindrops a negative charge, quite as definite and ordered as that for producing a positive charge on the drops; and, secondly, that there may be temporary, and perhaps local, conditions favouring the reception of drops of first one sign and then of the other. In this connexion an observation of Herath(12) is interesting; he found that the infrequent negative currents often coincided with a lull in the rainfall.

(*c*) *The courses of the rainfalls.* The results in table 3 suggest that there are various types of rainfall, with different courses, and the particular course will be determined by the agencies responsible for the charges on the raindrops and the prevailing meteorological conditions.

The most striking feature of table 3 is the nine examples of rainfalls with sequences of positively charged drops early and sequences of negatively charged drops later. In some of the rainfalls classified as "sequences of both signs", the percentage of positive charge is greater in the earlier part of the rainfall than later.

Simpson(21) in his first series of observations, found some indication of a similar result, but his later observations did not confirm this, and he finally concluded that there was no definite evidence that one sign predominated in any one part of a storm. McClelland and Nolan(17, 18) concluded that in some cases the occurrence of negative charge is associated with the latter part of a rainfall, but that this does not always hold. The present results agree with this conclusion, particularly in the case of continuous heavy rain.

(*d*) *The distribution in magnitude of the charges.* No previous observation has been able to give any result with which table 4 and figure 3 can be compared.

The general result of the analysis of the distribution is that we obtain a curve, figure 3, which is approximately symmetrical, with a maximum in the region of a small positive charge (about $0{\cdot}3 \times 10^{-3}$ e.s.u.). However, it would not be correct to imagine that the distribution is of the nature of an error function, for the results quoted above for the courses and sequences of sign show that in any one part of a rainfall we may have drops which fall mainly into one part of the distribution curve, while in another part of the rainfall, or in a separate rainfall may appear drops in another part of the curve. Moreover, in many of the separate rainfalls the distribution is far from symmetrical. This is true, in particular, of squall rain, storm rain and snow. Table 4 also shows that the spread of the distribution curves is greater in the more violent forms of rainfall, although it must be realized that this may possibly be due to the fact that more of the lightly charged drops might be missed in such cases.

It seems possible to reach the conclusion that, at any rate in ordinary rain, the charges on the drops are distributed symmetrically, and hence the distinction previously made (e.g. in the sequences) between positive and negative drops is not of great significance. In the more violent types of rain the distribution points do not fit so closely on a smooth curve, and it may be that factors operate which make the distribution more erratic; in particular may be noticed the steep fall on the negative side in the case of squall rain.

The preponderance of drops with small positive charges is related to the fact discussed above that the average positive charge is less than the average negative charge.

If the distribution curve is truly symmetrical, then we can estimate how many drops there are with charges from $-\frac{1}{4}$ to $+\frac{1}{4} \times 10^{-3}$ e.s.u. that have been missed by the present type of measurement; we see that the total should be about 2700, of which only 1021 were observed. It is interesting to note that the correction thus made to the average charges on positive and negative drops will still leave these considerably above the values obtained by Gschwend for ordinary rain (see table 7). Either Gschwend's large number of drops with small charges is incorrect, or else such drops must be additional to the distribution curve of figure 3, if this is kept as a symmetrical curve.

§6. GENERAL DISCUSSION OF RESULTS

It is not proposed to give, here, any attempt to account for the results that have been obtained, in terms of theories of the production of charges on water-drops. But it seems desirable to point out the significance of some of the results obtained from this and other work.

The general intermixing of positive and negative charges on raindrops suggests that one single process of separation of charge will not suffice to account for the results, but that it may be necessary to consider the drops to acquire their charges by at least two processes, which may be of different importance under different temporary and local conditions, giving rise to the sequences.

Interesting problems are raised in connexion with the question of the relation of the vertical potential gradient in the atmosphere to the charges on the raindrops; Benndorf(5) and Gschwend(10) state that often, but by no means always, the potential-gradient is of opposite sign to the drop-charges. Since the potential-gradient gives a measure of the charge residing in the lower side of the cloud or below this, it follows that the rain cannot merely bring down the charge of the cloud. On the other hand, if the rain obtains its charge by some process involving the separation of charge, then the negative charge left in the cloud or below, when positive rain falls, might be responsible for the negative potential-gradient often found.

Wilson ((23), p. 99) states that the arrival of a cloud without rain usually causes very little change in the vertical potential-gradient, so that there can be little charge resident in the cloud when there is no rain. But it has been found* that, at any rate sometimes, there are considerable charges resident in a cloud which is precipitating ordinary rain, and these usually consist of an upper positive and lower negative charge.

Gschwend(10) found very little correlation between drop-size and drop-charge, so that a theoretical account of the charges on raindrops cannot make use of the differences between drops of different sizes.

It may be pointed out that if the raindrops receive their charges in the cloud, then there must be a space-charge, normally positive, in the region below the cloud owing to the rain itself; this, by itself, would tend to give a potential-gradient of the same sign as the charge on the rain, and so we see that there must remain a larger opposite charge in the cloud. If, on the other hand, the rain receives its charge by processes below the cloud, the charge left in the air will move less rapidly than the raindrops and will give a space-charge of sign opposite to that on the rain, and will give rise to a potential-gradient such as is usually observed; but if there is a large separation of charge in the lower atmosphere, then we should expect an increase in the ionic conductivity, and those methods of measuring the vertical current in rainfall which include the ionic current, i.e. Herath's and Schonland's, should show an ionic current opposite in sign to the rain current; but, in fact, these two methods give the largest positive excess, and there is no evidence for an increase in conductivity in rainy weather. This point might be settled by an exact measurement of the space-charge below clouds during rain.

---

* We are indebted to Dr F. G. W. Whipple, of Kew Observatory, for informing us of the unpublished results obtained by the alti-electrograph in ordinary rain.

REFERENCES

(1) Baldit, A. *C.R. Acad. Sci., Paris,* **152**, 807–9 (1911).
(2) Baldit, A. *C.R. Acad. Sci., Paris,* **154**, 731–3 (1911).
(3) Baldit, A. *Radium, Paris,* **9**, 92–101 (1912).
(4) Banerji, S. K. *Philos. Trans.* A, **231**, 1–27 (1932).
(5) Benndorf, H. *S.B. Akad. Wiss. Wien,* **119**, 89–100 (1910).
(6) Berndt, G. *Phys. Z.* **13**, 151–2 (1912).
(7) Chalmers, J. A. and Pasquill, F. *J. Sci. Instrum.* **14**, 127–31 (1937).
(8) Elster, J. and Geitel, H. *Met. Z.* **5**, 95–8 (1888).
(9) Gerdien, H. *Phys. Z.* **4**, 837–42 (1903).
(10) Gschwend, P. *Beilage zum Jahresbericht der Kantonalen Lehranstalt in Samen* (1921–2).
(11) Gunn, R. *Terr. Mag.* **40**, 79–106 (1935).
(12) Herath, P. *Phys. Z.* **15**, 155–9 (1914).
(13) Kähler, K. *Veröff. K. Preuss. Met. Inst.* **213** (1909).
(14) Kohlrausch, K. W. F. *S.B. Akad. Wiss. Wien,* **118** (2), 25–69 (1909).
(15) Marwick, Miss T. C. *Quart. J. R. Met. Soc.* **56**, 39–44 (1930).
(16) McClelland, J. A. and Gilmour, A. *Proc. R. Irish Acad.* A, **35**, 13–29 (1920).
(17) McClelland, J. A. and Nolan, J. J. *Proc. R. Irish Acad.* A, **29**, 81–91 (1912).
(18) McClelland, J. A. and Nolan, J. J. *Proc. R. Irish Acad.* A, **30**, 61–71 (1912).
(19) Schindelhauer, F. *Phys. Z.* **14**, 1292–6 (1913).
(20) Schonland, B. F. J. *Proc. Roy. Soc.* A, **114**, 229–43 (1928).
(21) Simpson, G. C. *Philos. Trans.* A, **209**, 379–413 (1909).
(22) Weiss, E. *S.B. Akad. Wiss. Wien,* **115**, 1285–1320 (1906).
(23) Wilson, C. T. R. *Dict. of Applied Physics,* **3**, 84–106 (1923).
(24) Wormell, T. W. *Proc. Roy. Soc.* A, **117**, 567–90 (1929).

DISCUSSION

Dr D. Owen. It is interesting and surprising to realize that even in a smart shower of rain only a few drops fall in a minute into a receptacle having an aperture of about a square inch, so that the counting of charges on individual drops is not difficult. From the authors' data it appears that the maximum observed charge per drop, of either sign, amounts to about a hundred million electrons, and calculation shows that this is only about 1 per cent of the maximum charge that the dielectric strength of air at atmospheric pressure would permit, while the average raindrop holds only about one-thousandth of the maximum permissible charge. Perhaps the order of these values can be given some definite significance.

Dr F. J. W. Whipple. Observations of the charges on rain and snow must be regarded as fundamental in the development of any theory of atmospheric electricity. In the last few years numerous soundings have been made from Kew with the alti-electrograph, which records the sign of the potential-gradient, and it appears that there are at least two processes at work producing electrification in clouds.

Nearly all rain is melted snow, and in the upper part of a cloud where this snow occurs electricity is probably generated by the collision of the flakes. In the lower part of the cloud the snow flakes have become water drops and these, if they break up, will produce more electrification. Further, it is to be remembered that the charge on a drop will be changed during its descent through the ionized air between cloud and ground. It would be of the greatest interest to obtain information concerning the charges on drops in and just below the clouds. The method described by the authors might be employed in a balloon or at a mountain station, and it is to be hoped that they will endeavour to make further experiments under such conditions.

AUTHORS' reply. We do not at present see any definite significance in the values calculated by Dr Owen.

In reply to Dr Whipple: Our results would suggest that the two processes in the cloud are not sufficient; otherwise, results with snow, when only one process occurs, would be more simple than those with rain, and this is not the case in practice. It would seem that effects beneath the cloud are of importance, and they could be determined by observations in a balloon or at a mountain station, as Dr Whipple suggests. Information could also be obtained by simultaneous measurement of the potential-gradient.

THE MEASUREMENT IN ABSOLUTE UNITS OF THE INTENSITIES OF X-RAY REFLECTIONS FROM CRYSTALLINE POWDERS

By G. W. BRINDLEY, M.Sc., Ph.D., Mackinnon Student of the Royal Society, Physics Laboratories, University of Leeds

AND

F. W. SPIERS, Ph.D., Physicist, Radium Department, General Infirmary, Leeds

Received 30 *July* 1937. *Read in title* 8 *October* 1937

ABSTRACT. The two methods by which the intensities of X-ray reflections from fine powders can be measured absolutely by comparison with reflections from a standard substance are critically examined. The applicability of the mixture method is limited by the necessity for having powders of extremely small *particle* size, of the order of 10^{-5} cm. or less. In the substitution method, the powders are kept separate and the use of such fine powders is not essential; the absolute accuracy of this method is limited by the fact that the absorption coefficients of the two powders have to be known. Experimental results obtained by the two methods for powders of different particle sizes are compared with theoretical results by Schäfer for the effect of particle size on intensities measured by the mixture method. The agreement between the experimental and the theoretical results is sufficiently close to show the usefulness of Schäfer's analysis in determining the magnitude of the error which may occur when the mixture method is used with powders which are not sufficiently fine. A general account is given of a camera designed for use with the substitution method. It allows an alternating interchange of the two powders with a corresponding movement of the photographic film in order to obtain a separation of the photographs corresponding to the two powders.

§ 1. INTRODUCTION

The most usual and convenient method of obtaining the intensities of X-ray reflections from powders in absolute units is by comparison with reflections from some standard substance, such as NaCl, KCl or aluminium, for which absolute measurements have already been made by a single-crystal method; for reasons which will be discussed in detail elsewhere, we prefer to take finely powdered aluminium as the standard substance. The comparison may be made in two distinct ways. In one method the two powders are intimately mixed and irradiated simultaneously, while in the other the powders are separate and are irradiated alternately; these methods will be called the *mixture method* and the *substitution method* respectively. The actual form of the powder specimen may be either a flat plate or a cylindrical rod, but for intensity-measurements the flat layer has advantages over the cylindrical rod. In what follows we shall have in mind mainly the case of a flat layer, but usually our remarks will also be applicable to the other case.

The method of mixed powders has been developed and used extensively by Brentano(1–6) who has indicated in a series of papers the conditions which must be satisfied in order that the method may give accurate results. This method has also been used by Rusterholz(14) and by the present writers(7,8). There are, unfortunately, difficulties limiting its applicability which led the writers(9,10,11) and Brentano(4) to develop an arrangement in which the powders are irradiated separately and alternately and the photographs are separately recorded, although, as we shall show in § 2, the problems which confronted the writers and Brentano were of somewhat different types.

The purpose of the present paper is to review the factors which limit the accuracy of the two methods and to discuss the fields in which they may be used. Experimental results are compared, and it is shown that when differences occur they can be attributed to the unsuitability of the powders for use with the mixture method. Details of a camera for making accurate intensity-measurements by the substitution method are described also.

§ 2. GENERAL CONSIDERATIONS OF THE MIXTURE AND SUBSTITUTION METHODS

In discussing the two methods it will be convenient first to set down the expressions which relate the intensity of the reflected X rays to the crystallographic and geometrical factors of the flat powder block. It can be shown that the total energy I_r reflected from a flat stationary layer of powder of effectively infinite thickness is given by the following expression which was first given by Brentano(2) in a somewhat different notation:

$$I_r = C \frac{pN^2F^2\rho'}{\mu'\rho} \phi(\theta) A \qquad \text{......(1),}$$

where C is a constant, p is the multiplicity factor for the reflection, N the number of unit cells per unit volume of the crystal, F the amplitude scattered per unit cell, μ' the effective linear absorption coefficient of the powder block, ρ' the effective density of the powder block, ρ the true density of the substance itself, and $\phi(\theta)$ a trigonometrical function involving the glancing angle of reflection θ, which is such that $\phi(\theta) = [1 + \cos^2 2\theta]/\sin\theta \sin 2\theta$. Further, $A = \sin(2\theta - \alpha)/[\sin(2\theta - \alpha) + \sin\alpha]$, and allows for the fact that different reflections leave the powder at different angles, while α is the angle between the incident beam and the powder surface. The constant factor C involves the incident intensity, the wave-length of the radiation and electronic constants.

For a mixture of two very fine powders a common value can be assumed for μ'. If suffixes 1 and 2 then relate to the two components of the mixture it is easy to show that

$$\frac{I_1}{I_2} = \frac{p_1 F_1^2 \phi(\theta_1) A_1 G_1 v_2 M_2}{p_2 F_2^2 \phi(\theta_2) A_2 G_2 v_1 M_1} \qquad \text{......(2),}$$

where G denotes the weight of substance in the mixture, M is the molecular weight of the unit cell and v is the volume of the unit cell.

For the substitution method, we modify equation (1) by introducing the true linear absorption coefficient μ; since $\mu/\mu' = \rho/\rho'$ we can replace $\rho'/\mu'\rho$ by $1/\mu$. Then, using appropriate suffixes, we obtain for the ratio of the reflected intensities

$$\frac{I_1}{I_2} = \frac{p_1 N_1^2 F_1^2 \phi(\theta_1) A_1 \mu_2 t_1}{p_2 N_2^2 F_2^2 \phi(\theta_2) A_2 \mu_1 t_2} \qquad \text{......(3),}$$

where t_1 and t_2 are the exposure times for the two substances. In the light of these equations certain features of the two methods can now be discussed.

(*a*) *The mixture method.* The advantages and the limitations of this method have been very fully discussed by Brentano$^{(1-6)}$ in a series of papers in which he has developed it and only the main features will be set down here as concisely as possible. It is apparent from equation (2) that the intensities of two reflections, one from each substance, can conveniently be controlled by adjusting the factor G_1/G_2 which represents the proportions by weight of the components of the mixture. Since both substances are irradiated simultaneously and under identical conditions, fluctuations of X-ray output are of no consequence. The greatest advantage of the method, however, lies in the fact that the effective linear absorption coefficient can be taken to be the same for both components of the mixture, provided the powders are sufficiently fine, and in consequence the coefficient does not appear in equation (2). The method therefore requires no knowledge of absorption data, which, as will be seen later, is of considerable advantage. The powder particles must, however, be very fine (generally of the order of 10^{-5} cm. in diameter) and it was mainly this limitation which led the writers to develop an alternative method not requiring such very fine powders.

The mixture method is handicapped by the multiplicity of lines recorded from two substances simultaneously; it is often difficult, and perhaps impossible, if the substances have structures other than cubic, to find for comparison suitable pairs of lines which stand clear from neighbouring lines in a manner convenient for accurate photometry. Moreover, discontinuities in the background due to absorption jumps in the general radiation, which Brentano$^{(4)}$ has discovered, are more troublesome with a mixture of powders than with a single powder.* It was mainly with a view to avoiding superposition of lines and background discontinuities that Brentano developed a method of irradiating the powders separately.

(*b*) *The substitution method.* Equation (3) shows that in this method a ratio of exposure times replaces the mass-ratio of equation (2) and forms the means by which the reflections from the two powders are controlled to give lines of approximately the same density suitable for photometric comparison. The camera we shall describe later includes a simple mechanical arrangement for alternately raising and lowering a specimen-holder containing two flat parallel layers of powder, so that each powder is irradiated for a known period of time. Coupled with this movement of the powder-holder there is a corresponding movement of the photographic film so that the final result is a strip of film with two exposures, one from each powder, side by side for subsequent development under identical conditions. The exposures alternate at fixed intervals adjusted to suit the lines under comparison, so that in a total exposure of an hour or more slow fluctuations of the output of the X-ray tube become unimportant.

---

* *Note added in proof:* Since this was written, a paper by A. Baxter and J. Brentano has appeared, *Phil. Mag.* **24**, 473 (1937), which discusses these background discontinuities in detail.

A limit to the accuracy of this method arises from the appearance in equation (3) of the absorption coefficients of the two substances. The number of substances and wave-lengths for which accurate absorption data are available is very small, and in general it will be necessary to use an interpolation method to obtain the mass absorption coefficients of the component atoms. By far the most general method for interpolating absorption coefficients is that of Jönsson(13). Values of μ/ρ for commonly used wave-lengths calculated by Jönsson's method are given by W. L. Bragg in volume 1 of *The Crystalline State*. A comparison of these data with experimental values of μ/ρ, particularly those compiled by S. J. M. Allen and given in *X-rays in Theory and Experiment* by Compton and Allison, shows on the whole a close agreement; the differences are generally not greater than from 1 to 3 per cent. They are occasionally larger, but in many cases where larger differences are found the experimental values are more difficult to obtain, so that the discrepancies may be partly of experimental origin. On the whole it seems probable that the values of μ/ρ obtained by Jönsson's method are reliable to within 3 per cent except for light elements, such that $Z<10$, and long waves such that $\lambda>2A$, for which the error may be greater.

The substitution method is particularly suitable for another type of investigation for which the mixture method is ill suited, namely, the direct comparison of two powders of the same substance prepared in different ways. The absorption coefficients will then be the same for the two powders, and when a comparison is made between reflections with the same indices from the two powders, equation (3) reduces to

$$I_1/I_2=(F_1/F_2)^2\, t_1/t_2.$$

The authors(9,11) have used this method for comparing powders of distorted metals with chemically prepared powders of the same metals, and hence have obtained information as to the nature and magnitude of the distortion. The mixture method was first applied to this problem and gave very misleading results owing to the fact that the particles of filed metal were much too large to satisfy the absorption requirements of the mixture method.

§ 3. THE EFFECT OF PARTICLE-SIZE IN RELATION TO THE MIXTURE METHOD

The effect of particle-size on the X-ray intensities obtained by the mixture method has been considered by Schäfer(15). A simpler and somewhat different treatment has been given by Brentano(5). Both analyses agree in showing that for the method to give reliable results the particle-size must be so small that there will be negligible absorption in each particle. In practice this means that the particle-size must be of the order of 10^{-5} cm. or less. It is of interest to compare the deviations to be expected theoretically with those obtained experimentally when the particles are too large. Schäfer's expressions will be briefly stated here and applied to several examples which have arisen in our work and which illustrate the limitations imposed on the use of the mixture method by the absorption in the individual particles.

Consider the reflection of radiation by a particle X, figure 1, in a mixture of two powders, and let AX and XB be the directions of the incident and reflected radiations in the powder. Schäfer shows that the absorption along paths such as $(AX+XB)$ will be the same on the average, whatever kind of particle is at X. If dv is a volume element of the particle at X which is correctly oriented to reflect radiation, then the reflected intensity will be proportional to $e^{-\mu l}\,dv$, where μ is the linear absorption coefficient and l is the total path of the radiation in the particle. If every element of the particle reflects radiation, the total reflected intensity will be proportional to $\int_0^V e^{-\mu l}\,dv$, where the integration is over the volume V of the particle; the absorption therefore reduces the reflected intensity by the factor $V^{-1}\int_0^V e^{-\mu l}\,dv$.

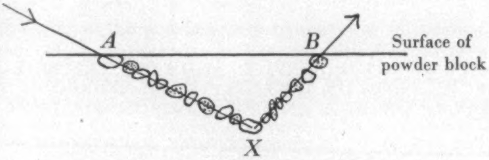


Figure 1

In general, however, only a fraction of each particle will reflect radiation, but if we take into account the fact that a large number of particles will be irradiated, then we can legitimately assume that on the average elements of volume reflecting radiation will be distributed equally in all possible positions in the different particles, so that the effect of absorption will still be to reduce the reflected intensity by the factor $V^{-1}\int_0^V e^{-\mu l}\,dv$. This will be strictly valid only if the particles are of the same size and orientation, a condition which can never be realized practically, but provided that the particles are of comparable size and devoid of any marked orientation, the expression will give an estimate of the order of magnitude of the effect.

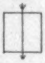
For a mixture, let I_1 and I_2 be the intensities reflected from the two substances. Then the effect of the particle-size of the powders on the ratio I_1/I_2 can be expressed by the ratio K, where

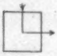
$$K=\frac{\text{observed ratio } I_1/I_2 \text{ for the actual mixture}}{\text{ideal ratio } I_1/I_2 \text{ for particles with negligible absorption}}.$$

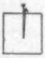
Alternatively,

$$K=\frac{[I_{\text{observed}}/I_{\text{ideal}}]_1}{[I_{\text{observed}}/I_{\text{ideal}}]_2}=\frac{V_1^{-1}\int_0^{V_1} e^{-\mu_1 l_1}\,dv_1}{V_2^{-1}\int_0^{V_2} e^{-\mu_2 l_2}\,dv_2}.$$

In the general case, K cannot be expressed more simply than by this equation, but by assuming particles of simple shape and orientation the integrals can be evaluated and the magnitude of K can be determinated. Schäfer has calculated the results for cubic particles of sizes D_1 and D_2 for angles $2\theta=0°$, $90°$ and $180°$. His results are as follows:

(*a*)  $2\theta=0°$ $K_0=e^{-\mu_1 D_1}/e^{-\mu_2 D_2}$

(*b*)  $2\theta=90°$ $K_{90}=\left\{\frac{1-e^{-\mu_1 D_1}}{\mu_1 D_1}\right\}^2\Big/\left\{\frac{1-e^{-\mu_2 D_2}}{\mu_2 D_2}\right\}^2$

(*c*)  $2\theta=180°$ $K_{180}=\left\{\frac{1-e^{-2\mu_1 D_1}}{2\mu_1 D_1}\right\}\Big/\left\{\frac{1-e^{-2\mu_2 D_2}}{2\mu_2 D_2}\right\}.$

§4. EXPERIMENTAL RESULTS SHOWING THE EFFECT OF PARTICLE-SIZE ON INTENSITIES MEASURED BY THE MIXTURE METHOD, AND COMPARISON WITH THEORY

Since in this work we are interested primarily in determining the amplitude F scattered per unit cell, it will be convenient to express Schäfer's ratio K in terms of F. Since the reflected intensity is proportional to F^2, we have

$$K=\frac{(F_1/F_2)^2 \text{ for the actual mixture}}{(F_1/F_2)^2 \text{ for particles with negligible absorption}}.$$

Since the particle-size difficulty is not present with the substitution method, we can find the value of (F_1/F_2) for particles having negligible absorption by using the substitution method, provided we select substances for which the absorption coefficients are known with sufficient accuracy. We may then write for K,

$$K=\frac{(F_1/F_2)^2 \text{ as obtained by the mixture method}}{(F_1/F_2)^2 \text{ as obtained by the substitution method}}.$$

In table 1 we give three experimental examples in which measurements were made first by the mixture method and secondly by the substitution method. In each case the experimental value of K is worked out and compared with that given by Schäfer's theory. Of course the agreement cannot be expected to be very exact, because each of the powders will consist of particles of various sizes and shapes, but the agreement is sufficiently good to indicate clearly the magnitude of the effect of particle-size on results obtained by the mixture method, and to show that Schäfer's expressions give a fairly reliable estimate of the degree of accuracy to be expected with any given mixture.

Table 1. A comparison of calculated and experimental values of K for various powder mixtures

				Calculated results				Experimental results	
	Powders	λ (A.)	μ	Particle-size (cm. × 10^{-4})	K_0	K_{90}	K_{180}	Estimated particle-size (cm. × 10^{-4})	K
Case I	KCl	1·54	247	KCl and Cu of equal size				KCl, 5	For Cu (111),
	Cu		471					Cu, 5	(200), (220)
				5	1·12	1·11	1·11		
				2	1·05	1·05	1·04		
				0·5	1·01	1·01	1·01		$K=1·00$
Case II	KCl	1·54	247	KCl, 5	2·27	2·10	1·97	KCl, 5	For Cu (111),
	Cu		471	Cu, 20				Cu, 20	$K=1·73$ (*a*)
									$K=1·56$ (*b*)
Case III	KCl	1·54	247	KCl and Ni, 5	1·09	1·08	1·08	KCl and Ni, 5	For Ni (200),
	Ni		413						$K=1·00$
	KCl	0·71	28·5	KCl and Ni, 5	1·22	1·22	1·21	KCl and Ni, 5	$K=1·29$
	Ni		429						

(*a*) Chill-cast copper. (*b*) Hard-drawn copper.

The particle-sizes of the powders were estimated by microscopic examination by viewing the particles against a scale engraved with divisions equal to 10^{-2} cm. In each case it was evident that the bulk of the powder by volume consisted of particles of about the same size. There appeared to be relatively few particles which were markedly larger. There were always present a large number of much smaller particles but these constituted only a small fraction of the total volume of the powder. In estimating the particle-size we have therefore taken an average value for the larger particles, since these form the bulk of the powder and it is on them that the success or failure of the mixture method will depend.

Each of the three cases given in table 1 brings out a point of interest. Case I shows measurements made on chemically prepared powders of KCl and Cu; the agreement between the mixture method and the substitution method is very close, as is seen by the mean value of K for three reflections of Cu measured with respect to KCl being equal to unity. The calculated values of K for equal-sized particles of various values are shown. The observed agreement between the two methods is therefore somewhat better than would be expected from the theory.

In case II, the copper particles were prepared by filing and sieving and are considerably coarser than in the previous example; the same KCl powder was used. The theoretical values of K indicate that large errors would be expected for such a mixture and this is in general agreement with the observed results. The experimental values of K measured for the 111 reflection of copper powder, filed (*a*) from a chill-cast copper rod, and (*b*) from a hard-drawn copper wire, are markedly greater than unity, though not so large as the calculated values.

Case III illustrates the fact that a mixture may be suitable for one radiation for which the powders have comparable values of μ but unsuitable for another radiation for which the μ's differ by a large factor. Thus chemically prepared nickel powder and KCl give satisfactory results by the mixture method when Cu $K\alpha$ radiation is used but not with Mo $K\alpha$ radiation. The experimental results in this case agree closely with the calculated values.

§ 5. THE EFFECT OF PARTICLE-SIZE AND CRYSTAL-SIZE ON THE MEASUREMENT OF X-RAY INTENSITIES

A clear distinction must be drawn between the effects of particle-size and of crystal-size on the accurate measurements of X-ray intensities. The particles of a powder will not usually be single crystals. With chemically prepared powders, the individual particles consist of clusters of smaller particles which may or may not be single crystals, unless a spacing material is used, as described by Brentano(5,6), which may be effective in preventing the adherence of the individual crystals to form composite particles. With mechanically produced powders, each individual particle will be an aggregate of much smaller crystals caused by distortion, cleavage and twinning.

The crystal-size of a powder affects X-ray reflections in several ways. In the first place, with extremely small crystals of colloidal dimensions (less than 10^{-6} cm.) there is a broadening of the reflected lines which makes the separation of adjacent lines from each other and of lines from the general background much more uncertain. Secondly, if the crystals are too large, of the order of 10^{-3} cm. or larger, the reflected lines are not continuous but consist of reflections from the individual crystals, and are quite unsuitable for photometry; furthermore, in such a powder too few crystals will be irradiated to satisfy the assumption of a random distribution of the reflecting planes. These two points are important in connexion with the accuracy of the actual measurements. The third point, namely the effect of extinction on the reflected intensities, is important in connexion with the interpretation of the results but has no effect on the accuracy of the measurements.

With powders, primary extinction only is likely to be operative, and this depends on the size of the crystals and on the amplitude reflected per plane in the crystal. Its importance will depend on the nature of the investigation; if it is of an atomic nature, such as the determination of an atomic scattering factor, then extinction should preferably be absent. On the other hand, if the investigation is concerned with a powder in a particular condition, then the intensities must be measured accurately for the powder in this state; the interpretation of the results may or may not be hindered by the presence of extinction.

The particle-size of a powder is important only in connexion with the use of the mixture method for obtaining absolute values, and is unimportant in connexion with the substitution method provided the particles are fine enough to give a specimen with a good surface—a condition which is easily satisfied, and which applies equally to both methods.

The limitation of the particle-size which is necessary in order that the mixture method may be satisfactory, implies also a limitation of the crystal-size to values of the same order as or less than the particle size, and for such small crystals primary extinction will usually be very small or negligible. This has been expressed by Brentano(5) in a slightly different way; presupposing that extinction is undesirable, he contends that the ideal aim is to reduce the particle-size so that extinction will be negligible even if the particles consist of single crystals, and there will then be no further difficulty in satisfying the absorption requirements. There is, however, the case of powders having a relatively large particle-size, of the order of 10^{-3} cm. to 10^{-4} cm., which are much too large for the mixture method, and containing much smaller crystallites of the order of 10^{-5} cm.; such powders are produced, for example, when metals and alloys are filed. This case has definitely been considered by Brentano(5) who has come to the conclusion that "with aggregate particles it is not safe to rely on their subdivision into uniformly small micro-crystallites", and states that he has observed "not only that in the case of ductile metals like gold, silver and platinum does the tendency exist for microcrystals to unite to larger crystallites, but also that in the case of brittle metals with a high temperature of recrystallization like tungsten some larger crystals are found embodied in the microcrystalline powder when no steps are taken to avoid the formation of large particles; the same thing was found with binary compounds like rock salt". Our own experience has led us to somewhat different conclusions. We have carried out experiments with filed silver and filed rhodium powders and find a large extinction effect; with filed copper and filed nickel powders(9), however, there is very little extinction, and it affects only the lower orders of reflection appreciably. With filed aluminium(12) we find no evidence for any extinction. These experiments suggest that with filed metals and alloys of the lighter elements there is little or no extinction.

The situation may be summarized as follows. The mixture method is only applicable when the particle-size is very small, of the order of 10^{-5} cm., and extinction will then usually be absent. The method is therefore limited to powders which can be produced in this extremely finely divided state and to experiments which are not dependent on the use of coarser particles. The substitution method is more generally applicable, since it does not necessitate the restriction of the particle-size to values of the order of 10^{-5} cm. and will give equally accurate values of the reflected intensities whether extinction is present or not. With regard to experiments which require elimination of extinction or its reduction to small values, the evidence so far available suggests that with heavier elements it will generally be desirable to reduce the particle-size to such small values that the mixture method will be applicable, but with lighter elements coarser particles, which may not be suitable for use with the mixture method, may be used. In actual practice there will always be a range of particle-sizes present in a powder, and in border-line cases, where one cannot be certain that the larger particles are not too large for use with the mixture method, it appears to be better to use the substitution method.

§ 6. AN X-RAY CAMERA FOR USE WITH THE SUBSTITUTION METHOD

Details of the camera are shown by sectional drawings to scale in figures 2*a*, *b* and *c*; subsidiary apparatus for interchanging the powder specimens is shown diagrammatically in figures 2*d* and *e*, which are not drawn to scale.

The camera consists primarily of a metal cylinder with a fine adjustable collimating tube pointing at the axis of the camera to define the incident beam of X-rays. The powder is mounted in a holder of rectangular or circular type so that the surface of the powder lies accurately on the axis of the camera. The reflections emerge through a horizontal slit in the wall of the camera and are recorded on a strip of photographic film wrapped in a holder and attached to the camera with elastic bands. One type of powder-holder, suitable for small quantities of powder, consists of two rectangular parallel cavities which are filled with the powders to be compared. When larger quantities of powder are available, a circular type of holder is used containing two annular cavities having dimensions corresponding to those of the rectangular cavities. This holder is kept in slow rotation in its own plane during the course of an exposure by means of a small motor; this type of holder not only has the advantage of allowing a much larger area of powder to be irradiated, but also makes the results largely independent of any minute imperfections in the powder-surface. The usefulness of the camera is greatly increased by having a number of identical and easily interchangeable specimen holders. A group of eight rectangular holders were machined out of a single bar of mild steel to ensure their having identical dimensions; these are bolted on to a brass metal plate attached to the main shaft of the camera. The circular holders are also interchangeable and are attached to the same brass plate; they are carried by a smoothly finished hollow cylindrical bearing passing through the centre of the brass plate.

The alternating interchange of the powders is effected by raising and lowering the central shaft of the camera by means of a cam *C* operated by the mechanism shown in figures 2*d* and *e*. This consists essentially of a large disc, made of 5-ply wood for the sake of lightness, about 1 ft. in diameter, through the edge of which are bolted two pins (one only is shown in figure 2*d*), at intervals apart suitable for the relative exposures required. The disc is driven by a $\frac{1}{12}$ h.p. synchronous motor through suitable gearing and makes approximately one revolution per minute. As the disc rotates, the pins make contact with four ball-shaped projections on the end of the shaft *S*, so that each time a pin engages one of these projections, the shaft is rotated through 90°; the arrangement is shown in greater detail in figure 2*e*. The other end of the shaft *S* carries the cam *C*, which consists of two similar projections; this is placed under the metal head *H* of the camera. Each quarter turn of the shaft *S* therefore alternately raises and lowers the central shaft of the camera, the movement being just sufficient to move one powder out of and the other powder into the X-ray beam. The relative exposure times are governed by the spacing of the pins. For most purposes it is sufficient to have twenty-four equally spaced holes round the circumference of the disc; if, for example, the pins are placed six

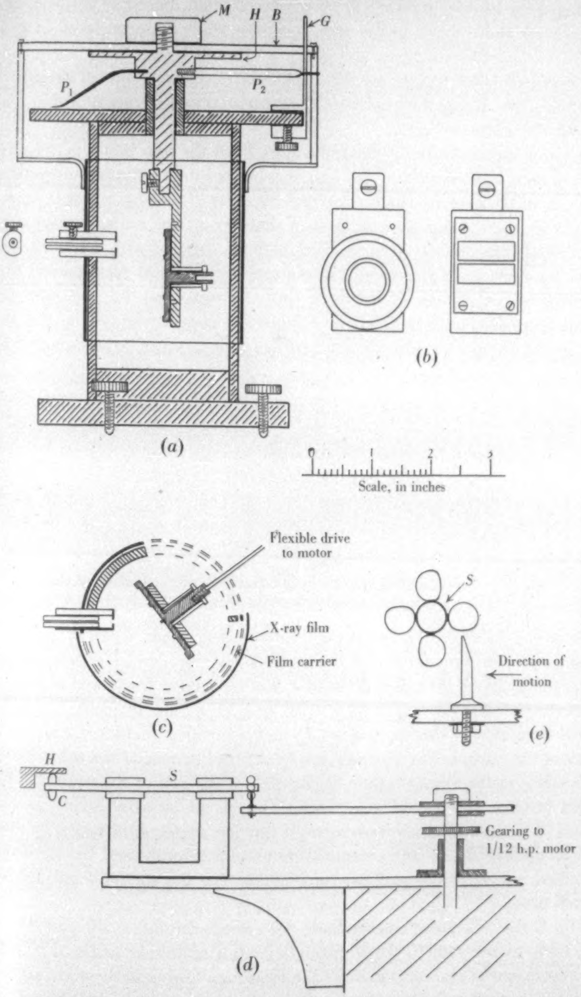

M
H
B
G
P_1
P_2
(a)
(b)
0
1
2
3
Scale, in inches
Flexible drive to motor
X-ray film
Film carrier
(c)
S
Direction of motion
(e)
H
S
C
Gearing to 1/12 h.p. motor
(d)

Figure 2. Details of camera and of subsidiary apparatus for interchanging the powder specimens. Figures (*a*), (*b*) and (*c*) are drawn to scale; figures (*d*) and (*e*) are diagrammatic.

holes apart, the powder holder will be in one position, raised or lowered, while six holes pass the shaft S and in the other position while eighteen holes pass, so that the ratio of the exposure times will be 1 : 3. In actual use we do not rely on this arrangement of holes to give us the correct ratio, but measure it directly with a clock at intervals during the exposure; the measured ratio agrees to within 1 or 2 per cent with the calculated ratio.

To avoid superposition of the reflections from the two powders, which would happen with a stationary film, the film is mounted on a cylinder surrounding the main body of the camera which is carried by a bar B passing across the top of the camera and firmly clamped to the central shaft by a large milled clamping-nut M. By this means, the movement of the film carrier is coupled with that of the powder-holder; the film, when developed, shows side by side two photographs from the two powders. A typical photograph—but over-exposed for the sake of good reproduction—is shown in figure 3; it shows a comparison of the 220 and 311 reflections of aluminium and the 420 and 422 reflections of potassium chloride.

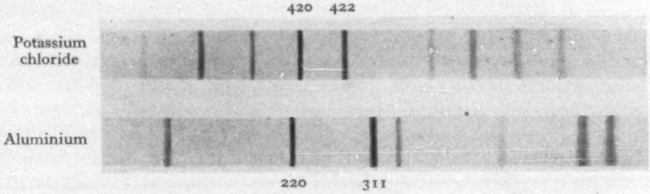


Figure 3. Typical photograph, showing comparison of potassium chloride and aluminium reflections.

Details of the top of the camera will now be described. When the milled nut M is unscrewed, the horizontal bar B to which the film carrier is attached and the central shaft carrying the powder holder, can be turned freely and independently. The setting of the powder-surface with respect to the incident X-ray beam is effected by means of the fine pointer P_1 moving over a graduated scale on the top surface of the camera. The setting is finally secured by means of a second pointer P_2 which slides in the vertical guide G clamped to the rim of the camera; this guide further ensures absence of any rotation when the powder-holder is raised or lowered. The up-and-down movement of the film carrier is obtained by its attachment to the bar B and any rotational movement is prevented by screwing down the milled nut M firmly and also, incidentally, by the slit rendered necessary by the collimator.

The X-ray reflections emerge from the camera through a slit $\frac{1}{4}$ in. wide in the main body of the camera which extends from a scattering angle of 0° almost to 180°; the extent of this slit is indicated in figure 2*c*. Owing to the vertical movement of the film carrier, it is necessary for the corresponding slit in the film carrier to be slightly more than $\frac{1}{2}$ in. wide; the difference between the two slit-widths is in fact equal to the vertical motion of the film which must also be equal to the distance between the centres of the two rectangular powder cavities. The circular powder holder is kept in rotation by means of a small motor connected by a very light flexible drive, which passes through a second slit in the wall of the camera as shown in figure 2*c*; this slit is made about $\frac{3}{4}$ in. wide in the camera and the corresponding slit in the film carrier is about 1 in. wide. The angular range of these slits is shown in figure 2*c*.

The details of the collimating system are shown on the left of figure 2*a*. It consists of a brass tube, $\frac{3}{8}$ in. in diameter, with a central hole of diameter $\frac{1}{8}$ in. into which suitable collimating tubes can be inserted. The side of the brass tube is cut away so that reflections can be recorded as nearly as possible up to 180°. A small screw holds the inner collimating tube firmly. We have found it most satisfactory to use fine collimating tubes made out of a lead-bismuth-antimony alloy (70 per cent lead, 15 per cent bismuth and 15 per cent antimony). As regards its absorption properties, this alloy is as satisfactory as pure lead and being much harder it has the advantage that it can be turned in the lathe and given a good finish. The edges of the brass cylinder are covered with lead foil, as also is the interior of the camera. A range of collimators has been constructed having diameters of 1 mm., $\frac{1}{2}$ mm. and $\frac{3}{8}$ mm., and lengths 2 cm., 1·5 cm. and 1 cm.

§7. ACKNOWLEDGEMENTS

Finally we would like to thank Dr J. Brentano for his readiness to discuss with us the various problems connected with the use of the two methods of measuring X-ray intensities from powders; our own views on the subject have been much clarified by the correspondence which has passed between us during the last two years. We also wish to thank Mr J. W. Spark, of the workshop staff of the laboratory, for his care in making the first camera of the type described in the paper. The camera eventually used was constructed by Messrs Reynolds and Branson, of Leeds, to the authors' design, the cost being defrayed out of a grant from the Government Grant Committee to one of us (G. W. B.).

REFERENCES

(1) Brentano, J. *Proc. Phys. Soc.* **37**, 184 (1925).
(2) Brentano, J. *Phil. Mag.* **4**, 620 (1927); **6**, 178 (1928).
(3) Brentano, J. *Z. Phys.* **70**, 74 (1931).
(4) Brentano, J. *Z. Phys.* **99**, 65 (1936).
(5) Brentano, J. *Proc. Phys. Soc.* **47**, 932 (1935).
(6) Brentano, J. and Baxter, A. *Z. Phys.* **89**, 720 (1934).
(7) Brindley, G. W. and Spiers, F. W. *Proc. Phys. Soc.* **46**, 841 (1934).
(8) Brindley, G. W. and Spiers, F. W. *Phil. Mag.* **20**, 865 (1935).
(9) Brindley, G. W. and Spiers, F. W. *Phil. Mag.* **20**, 882 (1935).
(10) Brindley, G. W. and Spiers, F. W. *Phil. Mag.* **20**, 893 (1935).
(11) Brindley, G. W. and Spiers, F. W. *Proc. Leeds Phil. Lit. Soc.* **3**, 4, 73 (1935).
(12) Brindley, G. W. *Phil. Mag.* **21**, 778 (1936).
(13) Jönsson, E. *Uppsala Univ. Årsskr.* (1928).
(14) Rusterholz, A. A. *Z. Phys.* **65**, 226 (1930); **82**, 538 (1933); *Helv. Phys. Acta*, **4**, No. 2 (1931).
(15) Schäfer, K. *Z. Phys.* **86**, 738 (1933).

THE KINETIC THEORY OF FLUIDS

By S. C. BRADFORD, D.Sc.

Received 9 *August*, 1937. *Read* 8 *October*, 1937

ABSTRACT: The kinetic theory is applied to the properties of real fluids by including the effect of molecular attraction. The observed properties of individual substances are calculated directly by pure dynamics from the attraction of their ultimate particles, thermal agitation and volume only, without the introduction of any arbitrary factors. The mutual attraction of the molecules of real substances increases their mean square velocity. Maxwell's law is modified by the introduction of a parameter λ which multiplies the most probable speed of the molecules, λ being the ratio of the most probable speed in a real fluid to that in an ideal gas. Other necessary consequences of molecular attraction are that all real gases and liquids are associated; there is at every interface an adsorbed layer which modifies the average effect of the transfer of momentum in collision, and there is a change of energy, due to variation of λ, in passing from one medium into another. These effects have been calculated. In order to apply the results, a law of force must be adopted. Edser's inverse-eighth-power law is found to hold. The method is applicable to all the physical properties of fluids and is applied, by way of example, to the equation of state of a gas and the vapour pressure and viscosity of a liquid with satisfactory results. The new theory explains the observed decrease of viscosity of liquids with temperature, without which no theory can be accepted.

§ 1. INTRODUCTION

The present paper, which extends the kinetic theory to real fluids, is developed on classical lines without any empirical assumptions, and it is shown that a very close approximation to the behaviour of real liquids may be obtained by a straightforward dynamical treatment, without recourse to quantum considerations such as those discussed by Lennard-Jones(1). The method developed does not depend on any particular law of force, but in order to test the formulae obtained, by comparison with experimental results some law of force is necessary. The law adopted is the inverse eighth power, deduced by Edser in a valuable paper contributed to the British Association Reports on Colloid Chemistry(2). The line of approach of the present paper differs from that adopted by Andrade(3), who considers the subject from the point of view of the solid state.

Maxwell's law of the distribution of molecular velocities is assumed. This is applied to molecules possessing attraction by the introduction of a parameter λ which governs the most probable speed of the molecules in a particular medium, λ being different for different media. This leads to a new theory of physics in which molecular attraction is as essential as is gravitation to astronomy, and the observed values of the properties of gases and liquids can be calculated directly from their coefficients of attraction. It is shown that all gases and liquids are associated in greater or less degrees.

The equation of state of a fluid,

$$A(p+K)(v-b)=\lambda^2RT,$$

is similar to that of van der Waals, except in including two essential new factors, A, the association, and λ. These explain the deviations of real gases from the old van der Waals equation and imply that low-temperature measurements are subject to serious error on account of the neglect of these terms, which become very important as the liquid state is approached.

The form of the factor representing transfer of momentum in collision is determined for liquids of changing density.

The cohesion, K, and the surface tension, S, of liquids having been evaluated as functions of the molecular attraction of their ultimate particles, a quantitative account of the phenomena of vaporization is given and the actual vapour pressures, boiling points, and viscosities of liquids are calculated directly from molecular attraction, volume and motion only, without the introduction of any arbitrary factors.

The formulae so deduced are applied to the calculation of the properties of elements and compounds, organic and inorganic, polar and non-polar, and ranging from the lightest gas to the heaviest liquid. The same methods are applicable to the whole field of molecular physics.

§ 2. MOLECULAR ATTRACTION

Molecular attraction is unquestionably the cause of the liquid and solid states. Lack of attention to this fact has been the cause of the failure of earlier attempts to establish a complete kinetic theory of liquids and gases. Such a theory must include a definite law of force. The law adopted here is Edser's inverse eighth power(2).

However, although it has been sufficient to adopt the simple law of force

$$f=\mu r^{-8} \qquad \text{......(2·1)}$$

in the present paper, it is necessary to recognize that molecules are electrically neutral, and that, while in some orientations they attract one another, in others they repel. The apparent resultant attraction may be due to the nearer approach, or longer duration, of the attractive encounters. The importance of molecular attraction is evident from the present paper. Attention should now be directed to deducing a complete law of force which will take into account the orientation of the colliding molecules and the differences in the nearest distances of approach in attractive and repulsive encounters. It should then be possible to extend the present theory to the consideration of the transition from liquid to solid, which depends on the fact that the attraction of solid particles, oriented in the most favourable position, is greater than that of liquid particles, which are able to assume any orientation. The physical properties of solids can then be calculated, and it may be possible eventually to include the treatment of chemical combination. In the meantime we must bear clearly in mind that the simple law of force mentioned above may not apply to the solid state.

§ 3. MAXWELL'S LAW IN THE CASE OF ATTRACTING MOLECULES

As Kleeman showed(4, 5), molecular attraction must make the average velocity of the molecules in a real substance greater than that in an ideal gas at the same temperature. In a real fluid a large number of moving points must exist, at which the instantaneous resultant of the molecular forces is zero. The velocities of molecules passing through these points are the same as in an ideal gas. But at other points the molecules are under the influence of the forces exerted by the surrounding molecules where, by the definition of force, their velocities cannot be the same as they would be if no forces were acting. It follows, therefore, that the average velocity of a molecule of a real substance is greater, and in the case of liquids and solids very much greater, than in an ideal gas.

In this paper it is assumed that the distribution of molecular velocities in a real fluid follows Maxwell's law, but with a different most probable speed α, which is greater than the most probable speed P in an ideal gas, as expressed by the equation

$$\alpha = \lambda P \qquad \text{......(3·1)},$$

where λ is a parameter of fundamental importance, expressing the ratio of the most probable speed of the molecules in a real fluid to that in an ideal gas at the same temperature. It will be seen that Maxwell's formulae in their original form are applicable to real fluids, provided that there is no change of phase. But in transition from one phase to another α is not constant.

Thus, the number of molecules of a real fluid which have the X component of their velocities between u and $u+du$ at any instant is

$$n_u = \frac{n}{\sqrt{\pi}\,.\,\lambda P}\, e^{-u^2/\lambda^2 P^2}\, du, \qquad \text{......(3·2)}$$

and so on. Similarly the average-kinetic-energy velocity C_r, whose square multiplied by half the mass of a molecule represents the average kinetic energy of a fluid, is given by

$$C_r^2 = \tfrac{3}{2}\alpha^2 = \tfrac{3}{2}\lambda^2 P^2 \qquad \text{......(3·3)}.$$

§ 4. TEMPERATURE

The realization of the fact that the most probable speeds of the molecules of real fluids at the same temperature are different leads to a new definition of temperature. Temperature Θ is now defined as the mean kinetic energy of a particle of an ideal gas in equilibrium with the substance under observation. Or

$$\Theta \equiv \tfrac{1}{2} m C^2 \qquad \text{......(4·1)}$$

$$= \tfrac{1}{2} m C_r^2/\lambda^2 \qquad \text{......(4·2)}.$$

The dimensions of temperature are therefore given by

$$[\Theta] = [ML^2T^{-2}] \qquad \text{......(4·3)}.$$

This definition gives a definite physical meaning to temperature and a clear insight into thermal changes, which can now be treated directly by means of the kinetic theory without the introduction of any thermodynamical methods.*

The following formulae follow immediately:

$$C^2=\frac{2\Theta}{m}, \qquad P^2=\frac{4}{3}\frac{\Theta}{m}, \qquad \alpha^2=\frac{4}{3}\frac{\lambda^2\Theta}{m}. \qquad \ldots\ldots(4\cdot4,\ 4\cdot5,\ 4\cdot6).$$

§ 5. MOLECULAR ASSOCIATION

Before passing to the deduction of the equation of state of a fluid it is necessary to consider one of the most important consequences of molecular attraction, i.e. association. There is considerable evidence that vapours do not condense to liquids, nor liquids assume the solid state, without passing through an intermediate stage in which the vapour or liquid particles are aggregated. It is, indeed, inconceivable that a gas could suddenly change into a liquid without assuming an intermediate condition in which its particles were associated. But association is not confined to the phenomenon of change of state. Having admitted the fact of molecular attraction we are forced to recognize that no real fluid, at any temperature, is unassociated. From the law of distribution of molecular velocities which has been adopted it follows that, at any temperature, always some pairs of molecules in collision will possess relative velocities that are less than the critical velocity required to overcome their mutual attraction. These pairs will become associated and remain in that condition until the association is broken by interaction with other molecules in the molecular chaos. In the noble gases, which have a very small cohesion, the critical velocity is also very small, and the number of associated molecules is almost negligible at ordinary temperatures and pressures. But, even these substances are considerably associated at low temperatures or high pressures. For all other gases molecular association is an essential fact under most conditions. An approximate formula for the association of a gas has been obtained by the methods of this paper. This formula has been used to calculate the values of association of the gases and vapours in table 1. A more accurate expression is now being deduced and will be communicated in a subsequent paper.

§ 6. THE EQUATION OF STATE OF A FLUID

Whatever be the law of molecular attraction, across any plane in the interior of a real homogeneous fluid there is a pressure K which is due to the mutual attraction of the particles of the fluid. This is termed the *cohesion* of the fluid. This pressure, together with the pressure p upon the walls of the containing vessel and the free surface of the fluid, is balanced by the expansion pressure p_e of the fluid particles moving across the plane. Or

$$p_e=p+K \qquad \ldots\ldots(6\cdot1).$$

---

* The quantity of heat U in a g.-mol. of an ideal gas is given by

$$U=\tfrac{1}{2}NmC^2=N\Theta.$$

In the case of a real fluid this becomes

$$U=N(1+\beta)\lambda^2\Theta \qquad \ldots\ldots(4\cdot5),$$

where β refers to the internal energy of the molecules.

The number of molecules per second, in unit volume of the liquid, having the components of their velocities normal to the plane between u and $u+du$ is

$$\frac{n}{\sqrt{\pi}\,.\,\alpha}\,e^{-u^2/\alpha^2}\,du.$$

The number of these that strike unit area of the plane per second will be this number multiplied by the speed u, i.e.

$$\frac{n}{\sqrt{\pi}\,.\,\alpha}\,e^{-u^2/\alpha^2}\,u\,du.$$

The partial pressure across the plane exerted by these molecules is their number multiplied by their change of momentum $2mu$. This pressure is, therefore,

$$\frac{2mu}{\sqrt{\pi}\,.\,\alpha}\,e^{-u^2/\alpha^2}\,u^2\,du.$$

The total pressure p_e is obtained by integration from $u=0$ to $u=\infty$. This gives

$$p_e=\tfrac{1}{2}mn\alpha^2 \qquad \ldots\ldots(6{\cdot}2).$$

Thus from equation (4·6) we obtain

$$(p+K)=\tfrac{2}{3}n\lambda^2\Theta \qquad \ldots\ldots(6{\cdot}3).$$

If v is the volume of 1 g.mol., we have

$$n=N/(v-b) \qquad \ldots\ldots(6{\cdot}4),$$

where

$$N=6{\cdot}06\times 10^{23} \qquad \ldots\ldots(6{\cdot}5),$$

and

$$b=\tfrac{2}{3}\pi\sigma^3N \qquad \ldots\ldots(6{\cdot}6)$$

$$=1{\cdot}30\sigma^3\times 10^{24} \qquad \ldots\ldots(6{\cdot}7),$$

σ being the average of the nearest distances of approach of the centres of two molecules in a great many collisions.

The formula (6·4) applies to all problems involving the transfer of momentum during collision of molecules in a homogeneous fluid. It may be written

$$n=\frac{N}{v}\cdot\frac{v}{v-b} \qquad \ldots\ldots(6{\cdot}8),$$

where $v/(v-b)$ will be termed the *collision factor*. In the sequel the form of this factor for a medium of varying density is obtained.

On the introduction of the association factor A, equation (6·3) becomes

$$(p+K)=\frac{2}{3}\,\frac{N}{A\,(v-b)}\,.\,\lambda^2\Theta \qquad \ldots\ldots(6{\cdot}9).$$

Transposing, we have

$$A\,(p+K)\,(v-b)=\lambda^2\mathrm{P}\Theta,$$

where P is a constant defined by the equation

$$\mathrm{P}\equiv\tfrac{2}{3}N \qquad \ldots\ldots(6{\cdot}10).$$

Changing from c.g.s. to centigrade units we obtain

$$A\,(p+K)\,(v-b)=\lambda^2RT \qquad \ldots\ldots(6{\cdot}11).$$

This is the equation of state of a real fluid. If it were possible to neglect the factors A and λ^2, the equation would be the same as that of van der Waals. It is now clear that his equation, although only approximate, was based on sound principles but could not represent the behaviour of gases and liquids accurately, because it neglected two important effects of molecular attraction.

The new equation represents satisfactorily the pressure, volume and temperature relations of pure gases and liquids. Nevertheless, we are not entitled to assume that it can be applied to the change from vapour to liquid and vice versa, because the energy transfers have not been considered. These changes will be investigated in the next section.

By writing $A=1$, $K=0$, $b=0$, and $\lambda=1$, the well-known Boyle's law is obtained

$$pv=RT \qquad \text{......(6·12).}$$

Since these last four equations are untrue, the method shows that Boyle's law does not apply to real fluids, and indicates very clearly the errors involved in thermodynamic analysis. By making the assumption that hydrogen obeys Boyle's law, we find

$$\Theta=5{\cdot}62\times10^{-14} \qquad \text{......(6·13)}$$

at 273° K., since

$$\mathrm{P}=4{\cdot}04\times10^{23} \qquad \text{......(6·14).}$$

The absolute zero of temperature on the c.g.s. scale is simply that at which molecules have no velocity of translation. Therefore $5{\cdot}6\times10^{-14°}$ E. are equivalent to 273° K., or

$$1^\circ\ \text{E.}=4{\cdot}86\times10^{15^\circ}\ \text{C.} \qquad \text{......(6·15),}$$

$$1^\circ\ \text{C.}=2{\cdot}06\times10^{-16^\circ}\ \text{E.} \qquad \text{......(6·16).}$$

This latter expression means that a centigrade degree is equivalent to $2{\cdot}06\times10^{-16}$ erg. We have also

$$\frac{\Theta}{T}=\frac{R}{\mathrm{P}}=2{\cdot}06\times10^{-16} \qquad \text{......(6·17).}$$

More exact figures derived from the equation of state will be communicated in a subsequent paper.

§ 7. VAPORIZATION AND CONDENSATION

Consider a pure liquid in equilibrium with its vapour only and maintained at a constant temperature Θ in a thermostat under ordinary laboratory conditions, so that any heat abstracted from the liquid by the escaping vapour will be supplied immediately by the enclosure, while any heat gained by the vapour will be given up to the surroundings.

At the common surface of the liquid and vapour there is a rapid gradation in density from that of the liquid to that of the vapour. In the first place, it will be assumed that in passing from the liquid to vapour and vice versa the density changes abruptly. The effect of the gradual change, which is very important, will be discussed in the sequel. The vapour of the liquid must be formed by particles that approach the surface of the liquid with the components of their velocities normal to the surface equal to or greater than a critical speed s which is sufficient to carry them through the surface of the liquid against the attraction of the liquid particles. The escaping particles are helped in their passage by the attraction of the vapour particles. But if the vapour is not dense this effect is inappreciable. The number of particles of the liquid striking unit area of the surface per second which have the components of their velocity normal to the surface equal to or greater than s is

$$n_l' = \frac{n_l \alpha_l}{2\sqrt{\pi}} e^{-s^2/\alpha_l^2} \qquad \ldots\ldots(7{\cdot}1),$$

where the subscript l refers to the liquid phase. Similarly, the total number of particles from the vapour that strike the same area of surface per second is

$$n_g' = \frac{n_g \alpha}{2\sqrt{\pi}} \qquad \ldots\ldots(7{\cdot}2),$$

the subscript g being used to indicate the vapour phase. The greater attraction of the liquid ensures that all these particles return to the liquid. In equilibrium, the number of particles escaping from the liquid must be equal to the number of those returning, or

$$\frac{n_l \alpha_l}{2\sqrt{\pi}} e^{-s^2/\alpha_l^2} = \frac{n_g \alpha_g}{2\sqrt{\pi}} \qquad \ldots\ldots(7{\cdot}3).$$

If, now, we consider the kinetic energy carried by the molecules in their passage to and from the liquid, we find that the total energy of all the molecules passing into the vapour per second through unit area of surface is

$$n_l' \left(\tfrac{1}{2}ms^2 + \tfrac{1}{2}m\lambda_l^2 P^2\right) \qquad \ldots\ldots(7{\cdot}4).$$

Of these molecules, one having its vertical component exactly equal to s would arrive at the surface with no kinetic energy. The energy $\frac{1}{2}ms^2$ represents the work done in escaping from the liquid. The remainder, i.e. $\frac{1}{2}m\lambda_l^2P^2$, is the average kinetic energy carried into the vapour by the capable molecules. Similarly, the molecules passing down from the vapour into the liquid bring with them the following kinetic energy per square centimetre per second:

$$\tfrac{1}{2}n_g' m\lambda_g^2 P^2.$$

Or, since λ_g is practically unity,

$$\tfrac{1}{2}n_g' mP^2 \qquad \ldots\ldots(7{\cdot}5).$$

In equilibrium the transfer of energy in both directions must be the same. Consequently

$$\tfrac{1}{2}m\lambda_l^2P^2 = \tfrac{1}{2}mP^2 \qquad \ldots\ldots(7{\cdot}6),$$

which gives

$$\lambda^2 = 1.$$

This simple arithmetic has been accepted as final evidence that the molecular forces do not affect the motions of molecules, which means that Newton's laws of motion apply in some cases and not in others. If this deduction were true, we might well accept the dictum that it is impossible to understand the physical construction of the universe. However, further inspection shows that the analysis has not been made to conform to the physical facts. We have not allowed for the variation of λ through the liquid-vapour interface. Particles entering the liquid from the vapour acquire kinetic energy additional to their temperature energy in the vapour state, on account of the attraction of the liquid particles. This energy is distributed through the liquid and is represented by the factor λ. Thus particles in the liquid possess, in respect of their λ, a certain kinetic energy in excess of the temperature energy corresponding to that of a perfect gas, and this energy is capable of doing work when the particles escape from the attractive forces. If we write W_λ as the average work that a particle can do in virtue of its λ in escaping from the liquid into the vapour, the total work W_v necessary to overcome the surface forces may be diminished by this amount in calculating s. Or,

$$W_s = W_v - W_\lambda \qquad \text{......(7·7).}$$

Referring again to equation (7·4) we see that, on an average, a particle passing through the surface from the liquid to the vapour contributes the energy it possesses on account of its λ towards overcoming the surface forces, and arrives in the vapour with the average kinetic energy $\frac{1}{2}mP^2$, and not $\frac{1}{2}m\lambda^2P^2$. The difference between these two quantities represents W_λ. Or,

$$W_\lambda = \tfrac{1}{2}mP^2(\lambda^2 - 1) \qquad \text{......(7·8).}$$

We see therefore that equation (7·6) is untrue and

$$\lambda^2 \neq 1.$$

We may now return to equation (7·3) from which, by substituting the values of n and α from (6·8) and (4·6), and putting

$$s^2 = 2W_s/m \qquad \text{......(7·9),}$$

we obtain

$$\frac{A_l(v_l - b)}{A_g(v_g - b)}\frac{\lambda_g}{\lambda_l} = e^{-W_s/\frac{2}{3}\lambda_l^2\Theta} \qquad \text{......(7·10).}$$

Now the behaviour of the vapour phase is represented by equation (6·10). Elimination of $A_g(v_g - b)$ between these two equations gives

$$p + K_g = \frac{\lambda_g\lambda_l \mathrm{P}\Theta}{A_l(v_l - b)}\, e^{-W_s/\frac{2}{3}\lambda_l^2\Theta} \qquad \text{......(7·11),}$$

or

$$p = \frac{\lambda_l \mathrm{P}\Theta}{A_l(v_l - b)}\, e^{-W_s/\frac{2}{3}\lambda_l^2\Theta} \qquad \text{......(7·12),}$$

since K_g and λ_g are comparatively very small.

It will be noticed that the first term in the expansion of the expression in the right-hand side of the last equation but one gives an equation similar to the equation of state, except that λ^2 is replaced by $\lambda_g\lambda_l$. It is clear that while the latter equation is true for a gas or vapour, it does not hold for a liquid which is giving off vapour.

In the vaporization expression it has been assumed that, for every liquid particle that approaches the surface in the state of aggregation corresponding to the degree of association in the liquid, a simple unassociated particle is transmitted to the vapour. In the present state of our knowledge it is impossible to determine whether these conditions hold exactly, or to allow for any energy-change involved in dissociation. There is, however, a further correction which can be introduced. As we have seen, the particles of the vapour must be associated. The number of particles which return to the liquid is

$$\frac{n_g \alpha_g}{2\sqrt{\pi}}.$$

The total mass of these particles is $A_g n_g \times m$, and their average most probable speed

$$\alpha_g = \frac{P}{\sqrt{A_g}} \qquad \text{......(7·13)}.$$

As, in equilibrium, the total masses of the escaping and returning particles must be the same, we have, omitting m from both sides,

$$\frac{n_l \lambda P}{2\sqrt{\pi}} e^{-s^2/\alpha_l^2} = \frac{A_g n_g . P/A_g^{\frac{1}{2}}}{2\sqrt{\pi}} \qquad \text{......(7·14)}$$

instead of equation (7·3). Consequently the vaporization equation (7·12) becomes

$$p = \frac{A_g^{\frac{1}{2}} \lambda_l \mathrm{P}\Theta}{A_l (v_l - b)} e^{-W_s/\frac{2}{3}\lambda_l^2 \Theta} \qquad \text{......(7·15)}.$$

Up to this point the analysis is independent of the law of force which governs molecular attraction. In order to apply the formulae to the behaviour of liquids it is necessary to deduce, from a definite law of force, the value of the cohesion of liquids and of the work done by escaping particles.

§ 8. THE ESCAPE OF A PARTICLE FROM A LIQUID

To find the attraction of the liquid on an escaping particle, let P_1 be the centre of a particle at a distance x below the surface AB of the liquid, where $x > \sigma$. The attraction of the particles of the liquid on P_1 may be taken as exerted by a continuous mass of liquid above AB. Particles in this supposed mass of liquid, whose centres would be between two planes parallel to AB, at distances ξ and $\xi + d\xi$ above AB, would exert on P_1 a resultant attraction equal to

$$\frac{2\pi n \mu d\xi}{(x+\xi)^6} \int_0^{\frac{1}{2}\pi} \cos^6 \theta \sin \theta \, d\theta$$

$$= \frac{2\pi n \mu d\xi}{7(x+\xi)^6} \qquad \text{......(8·1)}.$$

The total attraction on P_1 by all the particles whose centres would be above AB would be equal to

$$\frac{2\pi\mu n}{7} \int_0^\infty \frac{d\xi}{(x+\xi)^6},$$

which

$$= \frac{2\pi\mu n}{35 x^5} \qquad \text{......(8·2)}.$$

When the distance below the surface of AB of the escaping particle at P_2 becomes less than σ, that part above AB of a sphere with radius σ described around the particle would contain no centre of an attracting particle. The attracting molecules above AB may now be considered to have their centres within the portions above AB of two spheres with radii r and $r+dr$ described around the molecule at P_2. The resultant attraction on P_2 by molecules whose centres would lie between the surfaces of these spheres would be

$$\frac{2\pi\mu n dr}{r^6}\int_0^{\cos^{-1}(x/r)} \cos\theta \sin\theta \, d\theta$$

$$=\frac{\pi\mu n dr}{r^6}\left(1-\frac{x^2}{r^2}\right) \qquad \text{......(8·3)},$$

and the total attraction on P_2 by all the molecules whose centres would be above an imaginary sphere with radius σ would be

$$\pi\mu n\int_\sigma^\infty\left(\frac{1}{r^6}-\frac{x^2}{r^8}\right)dx,$$

which

$$=\pi\mu n\left(\frac{1}{5\sigma^5}-\frac{x^2}{7\sigma^7}\right) \qquad \text{......(8·4)}.$$

The work done by the molecule in escaping to the surface of the liquid is, therefore,

$$\frac{2\pi\mu n}{35}\int_{-\infty}^{-\sigma}\frac{dx}{x^5}+\frac{\pi\mu n}{\sigma^5}\int_{-\sigma}^{0}\left(\frac{1}{5}-\frac{x^2}{7\sigma^2}\right)dx,$$

which

$$=\frac{\pi\mu n}{6\sigma^4} \qquad \text{......(8·5)}.$$

An equal amount of work must be done by the molecule in escaping completely from the surface to infinity, so that the total work done by a particle of liquid in passing into the vapour is

$$W_v=\frac{\pi\mu n_l}{3\sigma^4} \qquad \text{......(8·6)}.$$

It should be noticed that the attraction of the vapour particles on the escaping particles has been neglected. It is easy to introduce the necessary correction, if desired, but at ordinary pressures this is not necessary. We can now determine the cohesion of a fluid.

§ 9. THE COHESION OF A FLUID

The cohesion K is defined as the attraction across an imaginary plane in the fluid exerted by all particles on one side of the plane for all the particles on the other side of the plane. Consider a plane AB drawn in the liquid. As in the previous section, the attraction exerted on any particle at a distance x below the plane, where $x>\sigma$, by all the particles on the other side of the plane is

$$2\pi\mu n/35x^5.$$

Therefore the attraction per unit area of AB exerted by all the particles above AB on all the particles below AB, whose centres are at distances greater than σ, is

$$\frac{2\pi\mu n^2}{35}\int_{-\sigma}^{-\infty}\frac{dx}{x^5}=\frac{2\pi\mu n^2}{140\sigma^4} \qquad \text{......(9·1)}.$$

Similarly, for particles at distances below AB that are less than σ, the total attraction per unit area is

$$\frac{\pi\mu n^2}{\sigma^5}\int_0^{-\sigma}\left(\frac{1}{5}-\frac{x^2}{7\sigma^2}\right)dx=\frac{16\pi\mu n^2}{105\sigma^4} \qquad \text{......(9·2).}$$

The total attraction across the plane, or the cohesion, is equal to the sum of the expressions (9·1) and (9·2), which gives

$$K=\frac{\pi\mu n^2}{6\sigma^4}=\frac{\pi\mu N^2}{6\sigma^4 v^2} \qquad \text{......(9·3).}$$

Similarly for a mixture or an associated fluid

$$K_{12}=\frac{\pi}{6}\left\{\frac{\mu_1^{\frac{1}{2}}n_1}{\sigma_1^2}+\frac{\mu_2^{\frac{1}{2}}n_2}{\sigma_2^2}\right\}^2 \qquad \text{......(9·4).}$$

§ 10. THE SURFACE TENSION OF A LIQUID

The surface tension may be determined very simply by Gauss's method: the surface tension S is equal to half the work W done per unit area of a surface AB described within a liquid in separating the liquid above AB from that below it. We have seen that the attraction of all the liquid molecules below AB on a molecule at a distance x above AB, where $x>\sigma$, is

$$2\pi\mu n/35x^5 \qquad \text{......(10·1).}$$

The work done in removing this molecule to infinity is obtained by integrating this expression multiplied by dx from x to ∞, which gives

$$\pi\mu n/70x^4 \qquad \text{......(10·2).}$$

Describe two planes parallel to AB at distances x and $x+dx$ above AB. Unit area of the liquid between these planes will contain ndx molecules. The work of removing these to infinity will be

$$\frac{\pi\mu n^2}{70x^4}\,dx \qquad \text{......(10·3).}$$

Therefore the work W_1 of removing to infinity the whole of the liquid molecules originally at a distance σ or more above AB is given by

$$W_1=\frac{\pi\mu n^2}{70}\int_\sigma^\infty\frac{dx}{x^4}$$

$$=\frac{\pi\mu n^2}{210\sigma^3} \qquad \text{......(10·4).}$$

When, however, the distance x of a molecule above $AB<\sigma$, the attraction on this molecule of all molecules below AB is

$$\frac{\pi\mu n}{\sigma^5}\left(\frac{1}{5}-\frac{x^2}{7\sigma^2}\right) \qquad \text{......(10·5).}$$

To remove this molecule from x to a distance σ requires an expenditure of energy equal to

$$\frac{\pi\mu n}{\sigma^5}\int_x^\sigma\left(\frac{1}{5}-\frac{x^2}{7\sigma^2}\right)dx,$$

which

$$=\frac{\pi\mu n}{\sigma^5}\left(\frac{\sigma-x}{5}-\frac{\sigma^3-x^3}{21\sigma^2}\right) \qquad \text{......(10·6).}$$

The work per unit area of AB necessary to remove to a distance σ all the molecules originally at distances between 0 and σ above AB is, therefore,

$$\frac{\pi\mu n^2}{\sigma^5}\int_0^\sigma\left(\frac{\sigma-x}{5}-\frac{\sigma^3-x^3}{21\sigma^2}\right)dx,$$

or

$$W_2=\frac{9\pi\mu n^2}{140\sigma^3} \qquad \text{......(10·7).}$$

Now the layer of liquid above AB comprises $n\sigma$ molecules per unit area of AB. The above is the work of removing these molecules to a distance σ above AB. The work of removing a single molecule from a distance σ to infinity is found by substituting σ for x in expression (10·2), which gives

$$\pi\mu n/70\sigma^4 \qquad \text{......(10·8).}$$

Therefore the work W_3 of removing $n\sigma$ molecules to infinity is given by

$$W_3=\pi\mu n^2/70\sigma^3 \qquad \text{......(10·9).}$$

Consequently the total work W of removing to infinity all the mass of liquid above AB is given by

$$W=W_1+W_2+W_3.$$

We have now created two surfaces of separation, one at AB and one at infinity. Consequently the energy S of one free surface is given by

$$S=\tfrac{1}{2}W,$$

or

$$S=\pi\mu n^2/24\sigma^3 \qquad \text{......(10·10).}$$

Similarly for a mixture

$$S=\frac{\pi}{24}\left\{\frac{\mu_1^{\frac{1}{2}}n_1}{\sigma_1^{\frac{3}{2}}}+\frac{\mu_2^{\frac{1}{2}}n_2}{\sigma_2^{\frac{3}{2}}}\right\}^2 \qquad \text{......(10·11).}$$

§ 11. THE EFFECTS OF VARYING DENSITY

In the previous discussion it has been assumed throughout that the density of the liquid changes abruptly at the surface to that of the vapour. Although the region through which this change takes place is very narrow, its thickness is considerable compared with the effective diameter of a molecule. There can be no doubt that within this region the change of density is not abrupt but continuous. It is now necessary to enquire how this gradual transition affects the calculations we have been making. So far it has not been possible to evaluate the change of density through the surface of a liquid. But Mr E. Lancaster-Jones has shown in the following lemma that, apart from the effect of the transfer of momentum during collision, which will be considered hereafter, the density-change does not affect the work done by a particle in escaping through the surface, provided the function expressing the variation of n is a continuous analytical function. Assume, therefore, that n is such a function of x, i.e.

$$n=f(x),$$

where x is the coordinate perpendicular to the surface of the liquid. We have also

$$f(-\infty)=0,$$

and $$f(+\infty)=n_l,$$

n_0 being taken as zero. Consider the force of attraction of the particles of the liquid on a particle at P in the surface of the liquid. Let the x coordinate of P be ξ, and consider a plate of liquid parallel to the surface at a distance h below P and of thickness dx. For the plate dx

$$x=\xi+h.$$

Firstly, figure 1, suppose that $$h<\sigma.$$

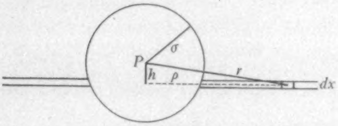


Figure 1.

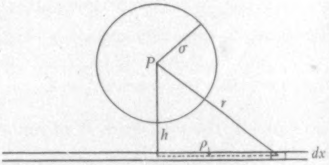


Figure 2.

The volume of a ring element dx of radius ρ is $2\pi\rho\,d\rho\,dx$, and this contains $2\pi f(\xi+h)\,\rho\,d\rho\,dx$ molecules. The coefficient of attraction being omitted, the force due to this element on the molecule at P, resolved perpendicularly to the surface of the liquid, is

$$2\pi f(\xi+h)\frac{\rho\,d\rho\,dx}{r^8}\times\frac{h}{r}.$$

Moreover $$r^2=\rho^2+h^2,$$

$$\therefore\quad r\,dr=\rho\,d\rho,$$

which gives the force due to the ring element as

$$2\pi f(\xi+h)\,h\,dx\,dr/r^8.$$

Therefore the total force F_1' on P due to the plate dx is given by

$$F_1'=2\pi f(\xi+h)\,h\,dx\int_{r=\sigma}^{\infty}\frac{dr}{r^8}$$

$$=\frac{2\pi}{7\sigma^7}f(\xi+h)\,h\,dx \qquad \text{......(11·1)}.$$

Secondly, figure 2, suppose that $h>\sigma$.

In this case the ring element is as before and the total force F_2' due to the slab is given by

$$F_2' = 2\pi f(\xi+h)\, h\, dx \int_{r=h}^{\infty} \frac{dr}{r^8} \quad .$$

$$= \frac{2\pi}{7h^6} f(\xi+h)\, dx \qquad \text{......(11·2)}.$$

Thirdly, the total force downwards on the particle at P due to the attraction of all the molecules below a plane through P is given by

$$\frac{2\pi}{7}(F_1+F_2),$$

where

$$F_1 = \int_{h=0}^{\sigma} \frac{f(\xi+h)\, h\, dh}{\sigma^7},$$

and

$$F_2 = \int_{h=\sigma}^{\infty} f(\xi+h) \frac{dh}{h^6},$$

since, in the equations (11·1) and (11·2), $dx = dh$, ξ being constant. This force is therefore

$$\frac{2\pi}{7}\left\{\frac{1}{\sigma^7}\int_{h=0}^{\sigma} f(\xi+h)\, h\, dh + \int_{h=\sigma}^{\infty} f(\xi+h)\frac{dh}{h^6}\right\}.$$

Consider F_1. Throughout the range of integration h is small, and we can put

$$f(\xi+h) = f(\xi) + hf'(\xi) + \frac{h}{2!} f''(\xi) + \dots + \frac{h^n}{n!} f^{(n)}(\xi+\theta\sigma),$$

a rapidly converging series, of which the terms after the first are relatively negligible.

Hence
$$F_1 = \frac{1}{\sigma^7}\int_{h=0}^{\sigma}\left[f(\xi)\, h\, dh + f'(\xi)\, h^2\, dh + f''(\xi)\frac{h^3\, dh}{2!} + \dots\right]$$

$$= \frac{1}{\sigma^7}\left[\tfrac{1}{2}\sigma^2 f(\xi) + \tfrac{1}{3}\sigma^3 f'(\xi) + \frac{\sigma^4}{4.2!} f''(\xi) + \dots\right]$$

$$= \frac{1}{2\sigma^5} f(\xi) + \frac{1}{3\sigma^4} f'(\xi) + \frac{1}{4\sigma^3.2!} f''(\xi) + \dots \qquad \text{......(11·3)}.$$

Next consider F_2. In the region beyond $h=\sigma$ we may imagine that within an interval from $h=\sigma$ to $h=\sigma+k$, where k is large compared with σ, the function $f(h)$ attains a value very nearly equal to n_l, its value at infinity. Beyond the plane $h=\sigma+k$ the function $f(h)$ changes very slowly and is always less than n_l.

Hence
$$F_2 = \int_{h=\sigma}^{k} f(\xi+h)\frac{dh}{h^6} + R_2,$$

where

$$R_2 = \int_{h=k}^{\infty} f(\xi+h)\frac{dh}{h^6}$$

and

$$|R_2| < \int_{h=k} n_l \frac{dh}{h^6}$$

$$< n_l \int_{k}^{\infty} \frac{dh}{h^6}$$

$$< \frac{n_l}{5k^5},$$

which is negligible in comparison with the effect of the region next considered. In this region where $\sigma \leqslant h \leqslant k$,

$$f(\xi+h)=f(\xi)+hf'(\xi)+\frac{h^2}{2!}f''(\xi)+\ldots+\frac{h^n}{n!}f^{(n)}(\xi+\theta h).$$

$$\therefore \int_{h=\sigma}^{k} f(\xi+h)\frac{dh}{h^6}=f(\xi)\int_{\sigma}^{k}\frac{dh}{h^6}+f'(\xi)\int_{\sigma}^{k}\frac{dh}{h^5}+\frac{f''(\xi)}{2!}\int_{\sigma}^{k}\frac{dh}{h^4}+\ldots$$

$$=\tfrac{1}{5}f(\xi)\left(\frac{1}{\sigma^5}-\frac{1}{k^5}\right)+\tfrac{1}{4}f'(\xi)\left(\frac{1}{\sigma^4}-\frac{1}{k^4}\right)+\frac{1}{3.2!}f''(\xi)\left(\frac{1}{\sigma^3}-\frac{1}{k^3}\right)+\ldots.$$

Since k is large compared with σ, and σ itself is very small we can put

$$F_2=\frac{1}{5\sigma^5}f(\xi)+\frac{1}{4\sigma^4}f'(\xi)+\frac{1}{3\sigma^3.2!}f''(\xi)+\ldots \qquad \ldots\ldots(11{\cdot}4),$$

where the terms rapidly diminish in magnitude.

Fourthly, the total force upwards on the molecule at P due to the attraction of all the molecules above the plane through P is given by

$$\frac{2\pi}{7}(F_3+F_4),$$

where

$$F_3=\frac{1}{\sigma^7}\int_{h=0}^{\sigma} f(\xi-h)\,h\,dh,$$

$$=\frac{1}{2\sigma^5}f(\xi)-\frac{1}{3\sigma^4}f'(\xi)+\frac{1}{4\sigma^3.2!}f''(\xi)-\ldots \qquad \ldots\ldots(11{\cdot}5),$$

and

$$F_4=\frac{1}{5\sigma^5}f(\xi)-\frac{1}{4\sigma^4}f'(\xi)+\frac{1}{3\sigma^3.2!}f''(\xi)-\ldots \qquad \ldots\ldots(11{\cdot}6).$$

Therefore, fifthly, the total resultant downwards force on the molecule at P due to all molecules above and below the plane through P is given by

$$\frac{2\pi}{7}F,$$

where

$$F=(F_1-F_3)+(F_2-F_4)$$

$$=2\left[\frac{1}{3\sigma^4}f'(\xi)+\frac{1}{5\sigma^2.3!}f'''(\xi)+\ldots\right]+2\left[\frac{1}{4\sigma^4}f'(\xi)+\frac{1}{2\sigma^2.3!}f'''(\xi)+\ldots\right]$$

$$=\frac{7}{6\sigma^4}f'(\xi)+\frac{7}{30\sigma^2}f'''(\xi)+\ldots \qquad \ldots\ldots(11{\cdot}7),$$

in which expression all the terms except the first can generally be neglected.

Therefore, the total resultant downwards force on the molecule at P is

$$\frac{\pi}{3\sigma^4}f'(\xi) \qquad \ldots\ldots(11{\cdot}8).$$

The work done by the molecule in traversing the liquid from the interior to the vapour is, therefore,

$$-\frac{\pi}{3\sigma^4}\int_{+\infty}^{-\infty} f'(\xi)\,d\xi \qquad \ldots\ldots(11{\cdot}9)$$

$$=-\left[\frac{\pi}{3\sigma^4}f(\xi)\right]_{+\infty}^{-\infty}$$

$$=\frac{\pi n_l}{3\sigma^4} \qquad \ldots\ldots(11{\cdot}10),$$

since it may be assumed that at the two ∞ points $f''(\xi)$, $f^{\mathrm{iv}}(\xi)$, etc., all vanish. This expression is the same as (8·6). Similarly, the transfer of momentum and kinetic energy depend only on the initial and final values of the density. However, in the above treatment we have neglected the effect of the transfer of momentum in collision on the work done by a molecule in escaping from the liquid. In a homogeneous fluid this effect is represented by the collision factor $v/(v-b)$. The effect in a medium of diminishing density is easily calculated.

In a homogeneous medium the work done by an escaping molecule must be multiplied by a collision factor F, where

$$F=(v-b)/v.$$

In each layer of the surface of a liquid of diminishing density the factor becomes F_1, where

$$F_1=(v_1-b)/v_1$$
$$=1-b/v_1,$$

b being constant, and v_1 the molecular volume in the layer. Since

$$n=N/v$$

and $$v_1=N/n_1,$$

where, as before, $$n_1=f(\xi_1),$$

we have $$F_1=1-b\,\{f(\xi_1)\}/N,$$

and the total work done by a molecule in traversing the liquid from the interior to the vapour becomes W_v, where

$$W_v=-\frac{\pi}{3\sigma^4}\left[\int_{+\infty}^{-\infty} f'(\xi)\,d\xi-\frac{b}{N}\int_{+\infty}^{-\infty} f(\xi)\,f'(\xi)\,d\xi\right] \qquad \text{......(11·11)},$$

instead of being given by the expression (11·9). On integration,

$$W_v=-\frac{\pi}{3\sigma^4}\left[f(\xi)-\frac{b}{2N}f^2(\xi)\right]_{+\infty}^{-\infty}$$
$$=\frac{\pi\mu}{3\sigma^4}\left[n_l-\frac{b}{2N}n_l^2\right].$$

Inserting the attraction coefficient μ and by means of equation (10·3), we have

$$W_v=\frac{2K}{n_l}-\frac{b}{N}K$$
$$=\frac{2Kv}{N}-\frac{Kb}{N}$$
$$=\frac{2K}{N}\left(v-\frac{b}{2}\right) \qquad \text{......(11·12)}.$$

Thus in a fluid of continuously diminishing density the collision factor becomes

$$\frac{v}{v-\frac{1}{2}b},$$

and $$n=\frac{N}{v-\frac{1}{2}b} \qquad \text{......(11·13)}.$$

This factor does not affect the cohesion of a homogeneous liquid, but it does influence the vapour pressure. The same factor must also be introduced into the expression (10·11) for the surface tension because the new surface created is such a region of varying density.

Consequently we have
$$S=\frac{\pi\mu N^2}{24\sigma^3 v^2}\cdot\frac{v-\frac{1}{2}b}{v} \qquad \text{......(11·14);}$$

and by comparison with equation (9·3) we have
$$K=\frac{4S}{\sigma}\cdot\frac{v}{v-\frac{1}{2}b} \qquad \text{......(11·15)}$$
$$=\frac{4\cdot331S}{b^{\frac{1}{3}}}\cdot\frac{v}{v-\frac{1}{2}b}\times 10^8 \qquad \text{......(11·16),}$$

from equation (6·7). If the liquid is associated, σ must be multiplied by $A^{\frac{1}{3}}$ and b by A.

§ 12. THE VARIATION OF DENSITY THROUGH THE SURFACE OF A LIQUID

We are now in a position to calculate the density of the liquid at any point in the surface. Let ξ_1 be the coordinate of the point, n_1 the molecular density, v_1 the molecular volume, K_1 the cohesion and λ_1 the coefficient of the most probable speed of the particles of the liquid at this point. The work W_1 done by a particle in escaping to this point is given by
$$W_1=-\frac{\pi}{3\sigma^4}\left[f(\xi)-\frac{b}{2N}f^2(\xi)\right]_{+\infty}^{\xi_1}$$
$$=\frac{\pi}{3\sigma^4}\left[n_l-n_1-\frac{b}{2N}(n_l^2-n_1^2)\right]$$
$$=\frac{2K_l}{N}\left(v_l-\frac{b}{2}\right)-\frac{2K_1}{N}\left(v_1-\frac{b}{2}\right) \qquad \text{......(12·1).}$$

Also, from equation (7·8)
$$W_{\lambda_1}=\tfrac{1}{2}mP^2(\lambda_l^2-\lambda_1^2) \qquad \text{......(12·2),}$$

and from equation (7·10)
$$\frac{(v_l-b)\lambda_1}{(v_1-b)\lambda_l}=e^{-W_s/\frac{2}{3}\lambda_l^2\Theta}.$$

Now the value of λ_1 in any particular layer is given by the equation of state (6·10), which provides a means of eliminating λ_1. Moreover, in the liquid state we may put $p=0$ as compared with K. So we get
$$\frac{\lambda_1}{\lambda_l}=\sqrt{\frac{(v_1-b)(p+K_1)}{(v_l-b)(K_l)}}.$$

And since, as we shall see, K is of the form a/v^2, we obtain
$$\left(\frac{v_1-b}{p+a/v_1^2}\right)^{\frac{1}{2}}=v_l\left(\frac{v_l-b}{a}\right)^{\frac{1}{2}}e^{W_{s_1}/\frac{2}{3}\lambda_l^2\Theta} \qquad \text{......(12·3),}$$

where all the terms except v_1 are known.

§ 13. ADAPTATION OF THE FORMULAE FOR CALCULATION

The formulae so deduced provide, for the first time, a practical means of calculating the physical properties of liquids and gases. For the attraction coefficient μ we have from equation (11·14)

$$\mu = \frac{24A^3\sigma^3 S v^3}{\pi N^2 (v - \frac{1}{2}b)} \qquad \text{......(13·1).}$$

With the aid of equation (6·7), this becomes

$$\mu = \frac{36A^3 b S v^3}{\pi^2 N^3 (v - \frac{1}{2}b)} \qquad \text{......(13·2)}$$

$$= 1{\cdot}639 A^3 S b v^3 (v - \tfrac{1}{2}b)^{-1} \times 10^{-71} \qquad \text{......(13·3).}$$

For the value K_d in dynes per cm.² of the cohesion K we obtain from equation (11·16)

$$K_d = 2{\cdot}642 \times 10^{79} \mu A^{-\frac{10}{3}} b^{-\frac{4}{3}} v^{-2} \qquad \text{......(13·41).}$$

The value K_a in atmospheres per cm.² is obtained by dividing by $1{\cdot}013 \times 10^6$, which gives

$$K_a = 2{\cdot}608 \times 10^{73} \mu A^{-\frac{10}{3}} b^{-\frac{4}{3}} v^{-2} \qquad \text{......(13·42).}$$

Apart from the A, these formulae are of the form

$$K = a/v^2 \qquad \text{......(13·5),}$$

as was supposed by van der Waals, where

$$a = \frac{2{\cdot}608\mu}{b^{\frac{4}{3}}} \times 10^{73} \qquad \text{......(13·6),}$$

its value now being known definitely. We have now all the material for adapting the gas equation and the vaporization formula (7·15). The former may be put into the form

$$p = \frac{\lambda^2 R T}{A(v-b)} - K \qquad \text{......(13·7)}$$

$$= 82{\cdot}06 \frac{\lambda^2 T}{A(v-b)} - K \qquad \text{......(13·8),}$$

where 82·06 is the value of R, corresponding to the pressure in atmospheres, obtained by dividing the centigrade c.g.s. value by $1{\cdot}0133 \times 10^6$.

Coming now to the development of the vaporization formula, it is convenient for the time being to omit A. Thus we have

$$W_s = W_v - W_\lambda$$

$$= \frac{2K}{N}(v - \tfrac{1}{2}b) - \tfrac{1}{2} m P^2 (\lambda^2 - 1) \qquad \text{......(13·9)}$$

$$= \frac{2K(v - \frac{1}{2}b)(v-b)}{N(v-b)} - \tfrac{2}{3}\Theta(\lambda^2 - 1) \qquad \text{......(13·10).}$$

Putting $$K(v-b)=\tfrac{2}{3}N\lambda^2\Theta, \qquad \text{......(13·111)},$$

since p is very small compared with K,

$$W_s=\frac{4\lambda^2\Theta\,(v-\frac{1}{2}b)}{3\,(v-b)}-\tfrac{2}{3}\Theta\,(\lambda^2-1) \qquad \text{......(13·112)}$$

$$=\tfrac{2}{3}\Theta\left\{2\lambda^2\left(\frac{v-\frac{1}{2}b}{v-b}\right)-\lambda^2+1\right\} \qquad \text{......(13·12).}$$

Comparison with equation (7·12) gives

$$p=\frac{\lambda P\Theta}{v-b}\exp\left[-2\,(v-\tfrac{1}{2}b)/(v-b)+1-1/\lambda^2\right] \qquad \text{......(13·13).}$$

By again making use of the relation

$$\lambda=\sqrt{\frac{K\,(v-b)}{P\Theta}} \qquad \text{......(13·14),}$$

in which p has been neglected as being very small compared with K, it is possible to remove λ completely from the vapour pressure formula. Thus from equation (11·16) we have

$$\lambda=2{\cdot}081\times10^4\sqrt{\frac{Sv\,(v-b)}{b^{\frac{1}{3}}\,(v-\frac{1}{2}b)\,P\Theta}}=2{\cdot}281\sqrt{\frac{Sv\,(v-b)}{b^{\frac{1}{3}}\,(v-\frac{1}{2}b)\,T}} \qquad \text{......(13·15),}$$

which gives

$$p=2{\cdot}081\times10^4\sqrt{\frac{SvRT}{b^{\frac{1}{3}}\,(v-\frac{1}{2}b)\,(v-b)}}\exp\left[-2\,\frac{v-\frac{1}{2}b}{v-b}+1-\frac{0{\cdot}192\,T\,(v-\frac{1}{2}b)}{Sv\,(v-b)}\right] \qquad \text{......(13·16).}$$

Giving R and e^{-1} their numerical values $8{\cdot}32\times10^7$ and $0{\cdot}368$, respectively, we obtain the vapour pressure p_d in dynes per cm.^{2} as:

$$p_d=6{\cdot}99\times10^7\sqrt{\frac{vST}{b^{\frac{1}{3}}\,(v-b)\,(v-\frac{1}{2}b)}}\exp\left[-\frac{v-\frac{1}{2}b}{v-b}\left\{2+\frac{0{\cdot}192\,Tb^{\frac{1}{3}}}{Sv}\right\}\right] \qquad \text{......(13·17).}$$

It is convenient to have this equation in the forms which give the values p_a, and p_{mm} of the vapour pressure in atmospheres and in millimetres of mercury respectively. These are obtained by dividing the equation by $1{\cdot}016\times10^6$ and by multiplying the result by 760. Thus, introducing the association factors A_g and A_l, we obtain finally

$$p_a=68{\cdot}8\sqrt{\frac{v_lSTA_g}{b^{\frac{1}{3}}A_l^{\frac{4}{3}}\,(v_l-b)\,(v_l-\frac{1}{2}b)}}\exp\left[-\frac{v_l-\frac{1}{2}b}{v_l-b}\left\{2+\frac{0{\cdot}192\,Tb^{\frac{1}{3}}}{Sv_lA_l^{\frac{2}{3}}}\right\}\right] \qquad \text{......(13·18)}$$

$$p_{mm}=5{\cdot}16\times10^4\sqrt{\frac{v_lSTA_g}{b^{\frac{1}{3}}A_l^{\frac{4}{3}}\,(v_l-b)\,(v_l-\frac{1}{2}b)}}\exp\left[-\frac{v_l-\frac{1}{2}b}{v_l-b}\left\{2+\frac{0{\cdot}192\,Tb^{\frac{1}{3}}}{Sv_lA_l^{\frac{2}{3}}}\right\}\right] \qquad \text{......(13·19).}$$

It will be seen that these formulae contain no unknown quantities except b and A. If we work with unassociated liquids, A can be neglected, leaving only b.

The sequel will show that b is constant except for a very small temperature contraction, which is compatible with a nearer mean distance of approach of the faster moving molecules at higher temperatures.

By taking into account the effects of the different attractions of two sets of molecules, it is obvious that the method can be applied to the solubility of gases in liquids and the miscibility of liquids. There is, however, a new effect in this connexion that will have to be considered, namely the effect of a foreign molecule on the cohesion and molecular volume of a liquid. When a molecule of solute, with, e.g., a smaller field of force than that of the solvent molecules, enters the solvent, the solute molecule must push apart the solvent molecules against their greater attraction, and vice versa. This means a change of molecular volume. The effect, which was indicated in a previous paper, is due to the difference in the attraction coefficients of the two sets of molecules. It is the reason why a liquid with less cohesion may not mix completely with another whose cohesion is greater. Actually the liquid with less cohesion is squeezed out of the denser liquid.

Similarly it is clear that the formulae can also be applied to the explanation of osmotic pressure. These phenomena will be treated in a subsequent paper. As an example of the wide application of the method, the theoretical part of this paper will be concluded by a discussion of the viscosity of liquids.

§ 14. THE VISCOSITY OF FLUIDS

This is particularly interesting as an instance of the fundamental importance of the collision factor, which, as will be seen, supplies the reason for the negative temperature coefficient of the viscosity of liquids. In dealing with viscosity, the force measured is that exerted between a moving fluid and a stationary solid. Momentum is transferred from the fluid to the solid through the adsorbed layer of intermediate density which must exist at the liquid-solid interface. As in previous sections, it is assumed that molecules behave as perfectly elastic attracting spheres. Collision takes place between individual molecules, whether the medium be gaseous, liquid or solid. At each collision the transfer of momentum obeys the ordinary laws of dynamics and molecules reflected from molecules forming the solid surface have such velocities as result from these laws.

Suppose the fluid to be moving with the mass velocity $\bar{u}$ in the direction OX, figure 3. We have to find the average momentum of the molecules crossing a plane $z=\zeta$ in the adsorbed layer between the homogeneous fluid and the stationary bounding solid, whose surface OX is at the plane $z=0$. The number of molecules crossing unit area of the plane $z=\zeta$ from the direction of the solid per second is

$$\tfrac{1}{4}n\bar{c} \qquad \text{......(14·1)},$$

where n is a function of z, say

$$n=f_1(z) \qquad \text{......(14·2)},$$

and $\bar{c}$ is given by

$$\bar{c}=4\sqrt{\frac{\lambda^2\Theta}{3\pi m}}\cdot\frac{v}{v-b} \qquad \text{......(14·3)}.$$

Now, as before,
$$\lambda^2 = \frac{K(v-b)}{P\Theta} \qquad \text{......(14·4).}$$

$$\therefore \quad \bar{c} = 2\sqrt{2}\,.\left(\frac{Kv^2}{\pi M(v-b)}\right)^{\frac{1}{2}} \qquad \text{......(14·5)}$$

$$= f_2(z), \text{ say} \qquad \text{......(14·6).}$$

The average mass velocity $\bar{u}$ in the direction OX of molecules crossing the plane $z=\zeta$ in both directions is also a function of z, or

$$\bar{u} = f_3(z) \qquad \text{......(14·7).}$$

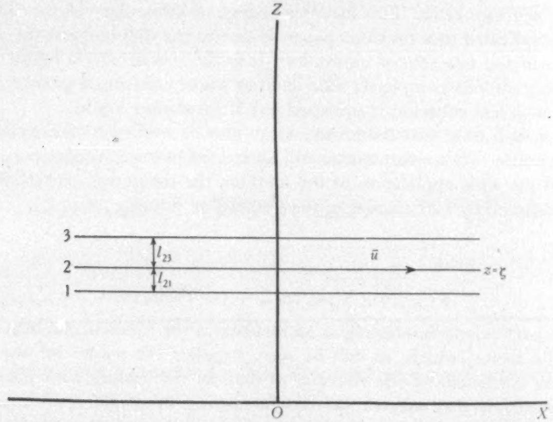


Figure 3.

Moreover, in treatises on the kinetic theory it is shown that the molecules crossing the plane $z=\zeta$ come from an average distance $\frac{2}{3}l$, where l is the mean free path and is given by the equation

$$l = \frac{1}{\sqrt{2}\,.\,\pi n\sigma^2} \qquad \text{......(14·8).}$$

or,
$$l = f_4(z) \qquad \text{......(14·9).}$$

But on account of the change in density of the fluid in the direction at right angles to the plane $z=\zeta$, the mean free path is different on different sides of the plane. Thus if l_{21} and l_{23} are the mean free paths in the directions of the liquid-solid interface and the pure liquid, respectively,

$$l_{23} > l_{21}.$$

The evaluation of these magnitudes, and their introduction into the equations of motion, leads to complications that it is impossible to consider in the present paper. It should be noticed, however, that, at both limits of integration the mean free paths are the same in both directions. Consequently, the omission of these details may not affect the result considerably. Returning to the argument, we note that the average momentum in the direction OX of a molecule in the plane $\zeta-\frac{2}{3}l_{21}$ is

$$mf_3(\zeta-\tfrac{2}{3}l_{21}) \qquad \text{......(14·10)}.$$

So that the total directed momentum per second carried across unit area of the plane $z=\zeta$ from the direction of the solid is

$$\tfrac{1}{4}mf_1(\zeta)f_2(\zeta)f_3(\zeta-\tfrac{2}{3}l_{21}) \qquad \text{......(14·11)}.$$

Similarly the directed momentum per unit area carried across the plane by all the molecules crossing from the direction of the pure liquid is

$$\tfrac{1}{4}mf_1(\zeta)f_2(\zeta)f_3(\zeta+\tfrac{2}{3}l_{23}) \qquad \text{......(14·12)}.$$

Since the directed momentum in the plane $z=\zeta$ is constant, the total momentum added from one side must be as much greater than the average for the plane as that added from the other side in less than the average momentum of the plane $z=\zeta$. This relation holds for each plane throughout the adsorbed layer until we reach the surface of the solid, which is a plane of no momentum. Here particles reaching the surface with the average momentum corresponding to the plane at a distance of two-thirds of one free path from it, are reflected from the surface with an equal momentum in the opposite direction. It is evident, therefore, that the surface may be supposed to act in the manner of a mirror, as is assumed frequently in problems of attraction, and the solid may be replaced by an imaginary fluid with diminishing density moving in the opposite direction and corresponding exactly to the mirror image of the adsorbed layer and the real fluid. The surface of the solid must be taken as that plane where the density is midway between that of the liquid and that of the solid.

We return now to the expressions (14·11) and (14·12). The former represents the total momentum per unit area added to the plane per second from one side, while the only molecules to which it is added come from the other side. Consequently the force acting on these molecules is represented by the difference between the expressions (14·11) and (14·12). This force X is equal to

$$X=\tfrac{1}{4}mf_1(\zeta)f_2(\zeta)\{f_3(\zeta+\tfrac{2}{3}l_{23})-f_3(\zeta-\tfrac{2}{3}l_{21})\} \qquad \text{......(14·13)}$$

$$=\tfrac{1}{4}mf_1(\zeta)f_2(\zeta)f_3'(\zeta)\{\tfrac{2}{3}l_{23}+\tfrac{2}{3}l_{21}\} \qquad \text{......(14·14)}.$$

Ignoring the inequality in the values of l, this last equation becomes

$$X=\tfrac{1}{3}mf_1f_2f_3'f_4 \qquad \text{......(14·15)}.$$

Now, from Newton's law, we have

$$\frac{X}{A}=\kappa\frac{d\bar{u}}{dz} \qquad \text{......(14·16)}.$$

And, since $A=1$, we find that

$$X=\kappa f_3'=\tfrac{1}{3}mf_1f_2f_3'f_4,$$

or

$$\kappa=\tfrac{1}{3}mf_1f_2f_4 \qquad \text{......(14·17)}$$

$$=f(n) \qquad \text{......(14·18)},$$

since f_1, f_2 and f_4 are all functions of n.

This expression shows that the value of κ in any plane parallel to the direction of flow depends on the average density and molecular diameter in that plane.

But in an experimental determination we measure the average effect of the transfer of momentum from the homogeneous liquid through the adsorbed layer to the surface of the solid. An average value $\bar{\kappa}$ of the viscosity is obtained by multiplying both sides of equation (14·17) by dn, integrating from $n=n_{sl}$ to $n=n_l$, and dividing by the integral of dn between the same limits. This gives the observed viscosity

$$\eta=\bar{\kappa}=\int_{n=n_{sl}}^{n_l} f(n)\,dn \Big/ \int_{n=n_{sl}}^{n_l} dn \qquad \text{......(14·19).}$$

To evaluate this expression we have

$$f(n)=\frac{2}{3}\frac{m}{\pi\sigma^2}\left\{\frac{Kv^2}{\pi M(v-b)}\right\}^{\frac{1}{2}} \qquad \text{......(14·20)}$$

$$=\frac{2}{3}\frac{M^{\frac{1}{2}}}{\pi^{\frac{3}{2}}N}\left\{\frac{Kv^2}{\sigma^4(v-b)}\right\}^{\frac{1}{2}}$$

$$=\frac{2}{3}\frac{M^{\frac{1}{2}}}{\pi^{\frac{3}{2}}N}\left\{\frac{a}{\sigma^4(v-b)}\right\}^{\frac{1}{2}} \qquad \text{......(14·21)}$$

$$=D\left(\frac{1}{v-b}\right)^{\frac{1}{2}} \qquad \text{......(14·22),}$$

where D is a constant. Therefore the integral in the numerator of equation (14·19) depends on

$$I=\int\left(\frac{1}{v-b}\right)^{\frac{1}{2}} dn,$$

since the other terms may be taken as constant.

Now $$n=\frac{N}{v}$$

and $$dn=-\frac{N}{v^2}\,dv,$$

so that $$I=-\int\frac{dv}{(v-b)^{\frac{1}{2}}\,v^2}.$$

By means of the substitution $$v-b=y^2$$

we get $$I=-2\int\frac{dy}{(y^2+b)^2},$$

and by putting $$y^2+b=r^2$$

we have $$I=-2\int\frac{dy}{r^4}.$$

This can be integrated by means of the formula

$$2b\int\frac{dy}{r^4}=\frac{y}{r^2}+\int\frac{dy}{r^2},$$

which gives
$$I=-\left\{\frac{y}{b\,(y^2+b)}+\frac{1}{b^{\frac{3}{2}}}\tan^{-1}\frac{y}{b^{\frac{1}{2}}}\right\}$$
$$=-\left\{\frac{(v-b)^{\frac{1}{2}}}{bv}+\frac{1}{b^{\frac{3}{2}}}\tan^{-1}\left(\frac{v-b}{b}\right)^{\frac{1}{2}}\right\}.$$

Consequently
$$\eta=D\,\frac{\dfrac{(v-b)_l^{\frac{1}{2}}}{bv_l}+\dfrac{1}{b^{\frac{3}{2}}}\tan^{-1}\left(\dfrac{v-b}{b}\right)_l^{\frac{1}{2}}-\dfrac{(v-b)_{sl}^{\frac{1}{2}}}{bv_{sl}}-\dfrac{1}{b^{\frac{3}{2}}}\tan^{-1}\left(\dfrac{v-b}{b}\right)_{sl}^{\frac{1}{2}}}{N\left\{\dfrac{1}{(v-b)_{sl}}-\dfrac{1}{(v-b)_l}\right\}} \qquad \text{......(14·23).}$$

When the properties of mixtures are treated in a subsequent paper, it will be shown that
$$\bar{\sigma}=\frac{\overline{m}^{\frac{1}{4}}}{\overline{n}}\left(\frac{n_1}{m_1^{\frac{1}{4}}}\sigma_1+\frac{n_2}{m_2^{\frac{1}{4}}}\sigma_2\right)$$
and
$$\overline{b}=\tfrac{2}{3}\pi\bar{\sigma}^3N$$
$$=\tfrac{2}{3}\pi N\left\{\frac{n_1}{\overline{n}}\left(\frac{\overline{m}}{m_1}\right)^{\frac{1}{4}}\sigma_1+\frac{n_2}{\overline{n}}\left(\frac{\overline{m}}{m_2}\right)^{\frac{1}{4}}\sigma_2\right\}^3.$$

With the aid of these expressions, together with (9·11) and (10·6), the above formula for the viscosity can be evaluated in the manner which follows. As will be seen, however, the application depends on a knowledge of K, v and b in the solid state. Conversely the formula could be used to determine the most probable values of these quantities by making use of available viscosity data extending over a wide range. The investigation is, however, too elaborate for this preliminary paper.

A simple and more manageable formula for the viscosity may be deduced by multiplying both sides of equation (14·17) by $f'(n)$, integrating as before and dividing by the integral of $f'(n)$ between the same limits. This gives
$$\eta=\bar{\kappa}=\frac{\displaystyle\int_{n=n_{sl}}^{n_l} f(n)\,f'(n)}{\displaystyle\int_{n=n_{sl}}^{n_l} f'(n)}$$
$$=\tfrac{1}{2}\{f(n_{sl})+f(n_l)\}. \qquad \text{......(14·24).}$$

To evaluate η we have
$$f(n)=\frac{2}{3}\frac{M^{\frac{1}{2}}}{\pi^{\frac{3}{2}}N}\left\{\frac{Kv^2}{\sigma^4(v-b)}\right\}^{\frac{1}{2}}$$
$$=GM^{\frac{1}{2}}F^{\frac{1}{2}}, \qquad \text{......(14·25),}$$
where
$$G=\tfrac{2}{3}/\pi^{\frac{3}{2}}N$$
$$=1{\cdot}98\times10^{-25} \qquad \text{......(14·26),}$$
and
$$F=\left\{\frac{Kv^2}{\sigma^4(v-b)}\right\} \qquad \text{......(14·27).}$$

Viscosity of a liquid. In this case we may write

$$f(n)_{sl} = f(n)_s^{\frac{1}{2}} f(n)_l^{\frac{1}{2}},$$

when we get

$$\eta_l = \frac{GM^{\frac{1}{2}}}{2} F_l^{\frac{1}{4}} (F_s^{\frac{1}{4}} + F_l^{\frac{1}{4}}),$$

where F_s is nearly constant for the material of the apparatus, since the temperature coefficient in the solid state is small compared with that in the liquid condition. Now, since

$$\sigma^4 = \left(\frac{3b}{2\pi N}\right)^{\frac{4}{3}}$$

$$= \frac{4{\cdot}331 S}{b^{\frac{1}{3}}} \cdot \frac{v}{v - \frac{1}{2}b} \times 10^8,$$

the factor

$$F_l = 4{\cdot}33 \left(\frac{2\pi N}{3}\right)^{\frac{4}{3}} \times 10^8 . \frac{Sv^3}{b^{\frac{5}{3}} (v-b)(v-\frac{1}{2}b)}$$

$$= H\left\{\frac{Sv^3}{b^{\frac{5}{3}} (v-b)(v-\frac{1}{2}b)}\right\},$$

where

$$H = 6{\cdot}00 \times 10^{40} \qquad \text{......(14·28).}$$

Thus the viscosity of a liquid becomes

$$\eta_l = \frac{GH^{\frac{1}{4}}M^{\frac{1}{2}}}{2} \left\{\frac{Sv^3}{b^{\frac{5}{3}} (v-b)(v-\frac{1}{2}b)}\right\}_l^{\frac{1}{4}} \left[\frac{F_s^{\frac{1}{4}}}{H^{\frac{1}{4}}} + \left\{\frac{Sv^3}{b^{\frac{5}{3}} (v-b)(v-\frac{1}{2}b)}\right\}_l^{\frac{1}{4}}\right]$$

$$= 2{\cdot}41 \times 10^{-5} M^{\frac{1}{2}} \left\{\frac{Sv^3}{b^{\frac{5}{3}} (v-b)(v-\frac{1}{2}b)}\right\}_l^{\frac{1}{4}} \left[\left\{\frac{Sv^3}{b^{\frac{5}{3}} (v-b)(v-\frac{1}{2}b)}\right\}_l^{\frac{1}{4}} + B_l\right] \qquad \text{......(14·29),}$$

where

$$B_l = F_s^{\frac{1}{4}}/H^{\frac{1}{4}} \qquad \text{......(14·30),}$$

and is practically constant for the material of the apparatus with a most probable value of 6·20. The form of this factor is important, because eventually it should be possible to use it in calculating the values of K and b in the solid state.

Viscosity of a gas. To calculate this we have

$$\eta_g = \tfrac{1}{2} (f_{lg} + f_g),$$

where the subscript *lg* refers to the fact that the greatly superior attraction of the solid particles must bring about the condensation of the gas at the solid surface in a state comparable to the liquid condition. Presumably this adsorbed layer is not more than one or two molecules in thickness, so that the measured diameter of the capillary tube is not affected. But the motion communicated to this condensed layer by the molecules of the gas which strike it will be inappreciable in comparison with that of the gas. Therefore the adsorbed layer and not the surface of the solid must be taken as the limit of integration in this direction. In the case of a gas we may write

$$f(n)_{lg} = \frac{f(n)_l + f(n)_g}{2}$$

and the above expression may be written

$$\eta_g = \frac{1}{2}\left\{\frac{f_l + 3f_g}{2}\right\}.$$

Now, since λ and $v/(v-b)$ become equal to unity in the gaseous state,

$$f(n)_g = \left(\frac{2}{3}\right)^{\frac{5}{3}} \frac{R^{\frac{1}{2}} M^{\frac{1}{2}}}{N^{\frac{1}{3}} \pi^{\frac{5}{6}}} \left\{\frac{T}{b^{\frac{4}{3}}}\right\}^{\frac{1}{2}}$$

$$= J\left\{\frac{T}{b^{\frac{4}{3}}}\right\}^{\frac{1}{2}}, \qquad \text{......(14·31)}$$

where

$$J = 2{\cdot}11 \times 10^{-5} \qquad \text{......(14·32)},$$

and, since

$$f(n)_l = GH^{\frac{1}{2}} M^{\frac{1}{2}} \left\{\frac{Sv^3}{b^{\frac{5}{3}}(v-b)(v-\frac{1}{2}b)}\right\}_l^{\frac{1}{2}},$$

we have

$$\eta_g = \tfrac{3}{4} J M^{\frac{1}{2}} \left[\left\{\frac{T}{b^{\frac{4}{3}}}\right\}^{\frac{1}{2}} + \frac{GH^{\frac{1}{2}}}{3J}\left\{\frac{Sv^3}{b^{\frac{5}{3}}(v-b)(v-\frac{1}{2}b)}\right\}_l^{\frac{1}{2}}\right]$$

$$= 1{\cdot}60 \times 10^{-5} M^{\frac{1}{2}} \left[\left\{\frac{T}{b^{\frac{4}{3}}}\right\}^{\frac{1}{2}} + B_g\left\{\frac{Sv^3}{b^{\frac{5}{3}}(v-b)(v-\frac{1}{2}b)}\right\}_l^{\frac{1}{2}}\right] \qquad \text{...(14·33)},$$

where

$$B_g = \frac{GH^{\frac{1}{2}}}{3J}$$

$$= 0{\cdot}80 \qquad \text{......(14·34)}.$$

When the values of b, v and K have been ascertained for the solid state, it will be possible to calculate the exact density of the condensed gas in the adsorbed layer. In the meantime, having regard to the comparatively enormous attraction of the solid, the most probable value of the density of the adsorbed layer is that of the liquefied gas at its melting point. By means of this supposition it is possible to calculate the value of $f(n)_l$ and, therefore, of the viscosity of a gas. It will be seen that the agreement between the calculated and observed values is very good.

In considering the viscosity of liquids, that of mercury is of peculiar interest. It has long been felt that the observed values obtained from experiments in glass tubes were too low. From the above analysis it is evident that if mercury slips through glass tubes the liquid-solid interface cannot be a surface of no motion, and therefore that the viscosity of mercury cannot be measured in this way. Tamann and Hinnüber recognized this fact and employed amalgamated copper tubes. The values calculated from the above formulae agree with their results and not with the figures resulting from experiments in glass tubes. Erk attempted to overthrow Tamann and Hinnüber's contention by suggesting that the increased viscosity was due to the formation of crystals of amalgam in the tube. But this supposition is incompatible with the fact that constant values were obtained. The theoretical considerations now adduced show that Tamann and Hinnüber were right, and supply an explanation of the anomalous low values of the viscosity of mercury obtained in glass tubes. The values of the calculated viscosities quoted in table 2 are correct within about 10 per cent throughout the enormous range from the lightest gas to the heaviest liquid. It will be seen that the viscosity of gases increases with temperature, as required, while the opposite effect is obtained for liquids, in accordance with observation.

§ 15. APPLICATIONS OF THE THEORY

The theory developed in the preceding pages affords a clear insight into the general behaviour of the ultimate particles, of which real gases and liquids are composed. By its means we are enabled to picture the manner in which the complicated motions and interactions of these ultimate particles produce, in the aggregate, the physical effects which we observe as the everyday properties of fluids. In order to test the theory, a few substances have been chosen for their likelihood of being least associated, since it is impossible to determine association in the liquid state at present. The substances cover all types of bodies, elementary and compound, organic and inorganic, polar and non-polar, and range from the lightest gas to the heaviest liquid. The closeness of the agreement between the calculated values and those obtained by experiment revealed in the following tables can only be described as remarkable.

(1) *Vapour pressure.* In table 1 are given the values of b calculated from the vapour pressure equation.

Table 1. Vapour pressures of liquid substances

Substance	Temperature T	Molecular weight M	Density ρ	Molecular volume v	Surface tension S	Apparent volume b of the molecules	Association of vapour A	Vapou pressu p (mm.
Hydrogen	15	2·016	0·0761	26·49	2·83	21·86	1·024	94·4
	20		0·0712	28·72	1·98	20·49	1·056	690
Ethyl ether	273	74·08	0·7363	100·6	19·1	85·5	1·016	185
	307·8		0·6960	106·4	14·7	84·8	1·029	760
n hexane	273	86·02	0·6787	126·9	20·5	111·0	1·010	46
	341		0·6148	140·1	13·4	110·8	1·032	745
Chloroform	298	119·5	1·476	80·97	26·2	69·3	1·014	203
	333·2		1·414	84·46	21·8	68·8	1·027	760
Phosphorus trichloride	273	137·4	1·613	85·21	29·3	75·5	1·006	38
	348·1		1·475	93·17	21·9	75·8	1·027	760
Mercury	373	200·6	13·35	15·03	452	14·14	1·000	0·3
	573		12·88	15·57	406	14·00	1·003	249

It will be seen that the values of b needed to give the observed vapour pressures are constant within 1 per cent, or less, except in the case of hydrogen. This is the first time that an equation of state has given constant values of b. It can hardly be doubted that the rather greater change in b calculated for hydrogen, is due in part to the difficulties of manipulation at very low temperatures, e.g. leakage of air. Moreover, the great change in the cohesion of liquid hydrogen, from $3{\cdot}88 \times 10^8$ at 15° to $7{\cdot}13 \times 10^8$ at 20° K., suggests that this substance may be greatly associated at the lower temperature, which is actually only just above its freezing point. It may be that the 8th-power law of attraction does not hold at very low temperatures. We need to know the physical cause of the law. It is also noteworthy that whereas b shows a slight contraction with rise of temperature in other cases, for phosphorus trichloride a small expansion is observed. This anomaly is almost certainly due to experimental difficulties, for the single determination of the surface tension made by Ramsay and Shields, i.e. 28·71 at 16·4°, does not fit the plotted results obtained by Jaeger which were used in this calculation.

The figures quoted in the above table demonstrate the fact that the vapour pressures and boiling-points of liquids are the results of molecular attraction, volume and motion alone; and since b can be determined by other means, e.g. from the viscosity equation, the vapour pressures and boiling-points of liquids can be calculated directly from first principles.

(2) *The {pressure, volume, temperature} relations of gases, and the correction of the thermometer.* The gas equation

$$A\,(p+K)\,(v-b)=\lambda^2RT,$$

contains two essential factors, A and λ, which were overlooked by van der Waals, and replaces his equation for the {pressure, volume, temperature} relations of gases. It is evident that the inclusion of these two factors suffices to give an account of these relationships, without variation of the apparent volume b of the molecules. In this formula the function K can now be calculated, and b is known from the vapour pressure formula, or otherwise. There remain the factors A and λ. An expression for calculating A will be communicated shortly. However, the latter factor is an implicit function of the other variables in the expression, and it can only be said that its value is the value which fits the equation. In the course of time, when a means has been found of calculating exactly the factor F_s in the viscosity equation, it will be possible to use this equation or that relating to another property of gases for calculating λ. We shall then have a means of completely determining the {pressure, volume and temperature} relations of gases and vapours.

(3) *Viscosity.* Table 2 gives the viscosities of the range of substances considered in this paper calculated by means of the formula (14·29) and (14·33), together with the observed values.

Table 2. Viscosities of gases and liquids

Substance	Temperature	Viscosity	
		Calculated	Observed
Hydrogen	273	0·000088	0·000087
	373	0·000096	0·000100
Ether	273	0·0032	0·0029
	307·8	0·0027	0·0023*
n hexane	273	0·0035	0·0040
	341	0·0026	0·0022*
Chloroform	298	0·0048	0·0054
	333	0·0039	0·0041*
Mercury	373	0·033	0·034*
	537	0·028	0·025*

* Extrapolated values.

It will be seen that the agreement between the calculated and observed values is sufficient to show that the viscosities of fluids can be calculated directly from first principles by means of the procedure developed in the present paper.

The methods of this paper can be applied to the whole field of molecular physics. The special case of water has not been treated here, because of its molecular complexity, but it is evident that it can be unravelled by the simultaneous consideration of several physical properties. It will then be possible to study the theory of solutions and steam. A preliminary investigation of the former has shown already that the depressions of the freezing points and the elevation of the boiling points of solutions of salts are due exactly to the greater attraction of the solid particles.

Throughout this paper the analysis has been made as simple as possible, in order to keep clearly in view the essential physical facts. For if these are obscured the most rigorous analysis can be of no utility. The central ideas have been the essential discontinuity of matter and molecular attraction.

REFERENCES

(1) LENNARD-JONES. *Proc. Phys. Soc.* **43**, 461–82 (1931).
(2) EDSER. British Association, *Fourth Report on Colloid Chemistry*, p. 40 (1922).
(3) ANDRADE. *Phil. Mag.* **17**, 497–511, 699–732 (1934).
(4) KLEEMAN, R. D. *Phil. Mag.* pp. 101–3 (1912).
(5) KLEEMAN, R. D. *A Kinetic Theory of Gases and Liquids* (1920).

DISCUSSION

Prof. W. WILSON: The author arrives at the conclusion "that the average velocity of a molecule of a real substance is greater, and in the case of liquids and solids very much greater, than in an ideal gas". I am sure he has in mind the case where the molecule of the real substance has the same mass as the molecule of the ideal gas, and so he violates the principle of equipartition. Now I maintain that this principle is an inevitable consequence of the classical premises from which he professes to start out.

He is mistaken in supposing his definition of temperature (4·1) to be new. He will find a more complete statement of the same definition in the chapter on temperature in Max Planck's *Thermodynamik* and also in my work on *Theoretical Physics*, **1**, 223.

My last criticism is a minor one. The dimensional equation (4·3) is erroneous. There is in it an error of precisely the same type as that contained in

$$Q=M^{\frac{1}{2}}L^{\frac{3}{2}}T^{-1},$$

where Q, M, L and T are respectively electric charge, mass, length and time.

Prof. ANDRADE: I have been much impressed by the care and labour which the author has put into his ambitious attempt to build up an embracing theory of fluids. I am still of the opinion that the right way of approaching liquids is from the solid, rather than from the gaseous, point of view, but no doubt valuable work can be done from the latter aspect. There are, however, one or two points about the paper that trouble me considerably. It seems to me that the author's fundamental assumption, "that the average velocity of a molecule of a real substance is greater, and in the case of liquids and solids very much greater, than in an ideal gas", leads at once to grave difficulties, especially in view of his acceptance of the Maxwellian distribution law. Both Maxwell's law and the equipartition of energy follow from classical mechanics, on which, I understand, the author bases his theory. Yet if we accept the equipartition of energy his fundamental assumption is impossible. It would, for instance, lead to a value of the molecular specific heat for solids and liquids very much in excess of the experimental values. In any case, I see no reason for the statement that the velocities of molecules passing through a force-free point must be the same as in an ideal gas. The velocity in a force-free space is, of course, entirely dependent on the previous history of the particle.

I further find difficulties in his whole treatment of liquid viscosity. There is no doubt that there is no slip of a liquid at a solid surface, even in the case of liquids which do not wet the solid. Very extensive experiments have been carried out on this point. To take the case of mercury, which he quotes in particular, determinations of the viscosity by the flow through glass capillaries have been made by at least six observers, all of whom assume Poiseuille's law with no slip, and arrive at about the same value for the viscosity. The radii of the tubes used in the different experiments vary from 0·053 to 0·406 mm. If there were actually slip the values given by applying Poiseuille's law would show a large and systematic variation with radius. Bénard, in particular, in his measurements on mercury, went carefully into the question of an upper limit for the slip and showed that, even if it existed, it must be equivalent to something less than an increase of the diameter of the tube of 0·001 mm., which is, of course, beyond the limits of the measurement of radius.* Further, Fawsitt made measurements by a completely different method, namely that of the oscillating disc, using four different discs, of two different materials, and obtained values which not only were self-consistent, but also agreed very well with the capillary-tube values. If there were slip, these values, based on formulae which assume no slip, could not possibly show this degree of agreement. There seems no doubt that the values of Tammann and Hinnüber, carried out with a copper tube, were vitiated by the silting up of the tube in some way as a result of the action of the mercury on the copper, leading to the growth of either crystals or a sheet of amalgam.

If, now, we accept the consistent values found for glass capillaries and for iron and glass oscillating discs, we must substitute for the values which the author gives as "observed for mercury" viz. 0·034 and 0·025, at 100° c. and 264° c. respectively, other values, namely, 0·0124 and 0·0098, which are about a third of his calculated values. Further, the temperature coefficient of liquid viscosity given by his formula differs greatly from the experimental values. Another point that troubles me is the increase with temperature of the association of all the vapours given in his table 1. This seems very hard to reconcile with current ideas.

---

* Brillouin, *Leçons sur la Viscosité*, 1, 158.

Returning to the question of slip at solid surfaces, there seems no reason why, quite apart from the experimental results, lack of wetting should imply slip. Slip is, after all, a question of the liquid-solid interface, while wetting further involves a gas surface. As a matter of fact Dr Greenland has shown, in my laboratory, that perfectly pure mercury does wet clean quartz glass. The fact that a mercury seal can preserve a vacuum unchanged for years seems conclusive proof that there is no faulty contact between the mercury and the glass. A very simple experiment that I have just carried out makes the lack of slip visible at once. A flat drop of mercury is put on a glass plate and a little dust is sprinkled on it. If the plate is then inclined, the drop will run down it, and from the dust it can be seen that this motion takes place by the mercury at the top of the drop running forward, while that in contact with the glass remains at rest.

If, however, I am unable to accept the author's treatment of liquid viscosity, in which, apparently, the interaction between the liquid and the solid surface plays so prominent a part, it is not to say that I do not find his paper very suggestive as to lines along which results may be sought.

Dr H. CHATLEY: This paper attempts to realize an ambition which I myself aimed at in my six papers on cohesion and molecular force presented to the Society. The whole question is whether or not a parabolic force formula can be made the basis of a theory of matter. Edser considered such a formula to be only a statistical and empirical generalization, and it may be questioned whether the author has really done more than confirm Edser's views. The author's basic equation of state includes three unknowns A, b and λ and so permits a considerable degree of discretionary adjustment to data. What view does the author take of the force law, within what range is it sufficiently exact, how can it be related to the actual multipolar structure of the molecules and their rotations, and how can its application to the solid state be envisaged?

AUTHOR's reply. In regard to Prof. Andrade's opinion that the subject is best approached from the point of view of solids, I would point out that the method adopted is a general one and should apply to gases, liquids and solids. The paper is an attempt to calculate the properties of matter from attraction, volume and motion. However, there can hardly be any doubt that both liquids and gases differ from solids in possessing an additional degree of freedom. The molecules are able to rotate. The law of force adopted applies to this state, and it may not apply to the solid state, in which the orientation of the particles is more or less fixed. The assumption of a greater average kinetic energy of the molecules of a real substance is essential to the paper. Equipartition is a consequence of Maxwell's law of distribution and holds only for a perfect gas. I maintain that molecular forces must alter the average kinetic energies of the molecules. At the same temperature, the mean kinetic energies of the molecules of different substances, or phases of substances, are different, according to the molecular forces existing. If this is true, the law of equipartition falls to the ground. My theory is based on Maxwell's law of distribution, with the addition of this necessary consequence of Newton's laws of force. It is therefore truly classical in its basis. This answers Prof. Wilson's criticism also.

Prof. Andrade's contention that the velocities of molecules passing through transitory force-free points are not necessarily the same as they would be in an ideal gas of the same molecular weight appears to be sound. The statement in my paper was quoted from Kleeman's paper$^{(4)}$. It is not essential to my thesis.

The theory does not necessarily lead to higher values of the specific heats of metals, because the principle of equipartition does not hold.

The explanation of the difficulty in regard to the viscosity of mercury is simple. Calculations of slip are based on empirical hydrodynamical considerations of internal friction, etc., which take no account of the discontinuity of matter or of the various effects of molecular attraction discussed in this paper. The actual effects on the radii of the tubes are due to thin adsorbed films, probably not of great thickness, and quite beyond the range of physical measurement. The fact that the observations involving slip in tubes of different diameter give consistent results is not necessarily a contradiction of my theory. The experiment which Prof. Andrade describes proves that the surface of a drop of mercury in contact with a glass plate moves less slowly than the drop. According to my theory, there is a very strong attraction between the molecules of the two substances, which ensures very close contact, if allowed. Even slight irregularities would produce the effect observed. Actually the mercury is rolling in adsorbed filth. In a capillary tube the effect need not be the same. This attraction of the particles is the cause of the sealing effect of mercury referred to. Molecules of air can penetrate between the glass-mercury interface only by possessing sufficient energy to overcome the cohesion of the surfaces, which they practically never do.

The considerations which I have introduced into the discussion of viscosity are the necessary result of molecular attraction. The formula developed is approximate but I have shown how a more accurate formula may be deduced. Doubtless further modifications will be found to be necessary. But this is the first time that the observed viscosities of liquids, with temperature coefficients of the right sign, have been calculated from first principles. I prefer to accept the values of the viscosity of mercury indicated by my theory as giving the explanation of a long-felt difficulty.

The small temperature-increase in the association of all vapours quoted is due to the great increase in the vapour density. This will be clear when the association formula is published.

The difference between my definition of temperature and that of Prof. Wilson is that I have identified temperature with energy, while Prof. Wilson defines a scale of temperature in which temperature appears as the product of pressure and volume divided by the gas constant, so that

$$T=\frac{pv}{R}.$$

Both definitions may lead to the same results, but my definition is the only one which can give a clear physical conception of the nature of temperature. The difference between the two definitions is illustrated by Prof. Wilson's doubt about the truth of my dimensional formula for temperature, which is an inevitable consequence of my definition.

As Dr Chatley remarks, my paper confirms Edser's views that the properties of matter are the result of molecular attraction, and that the force of attraction varies inversely as the eighth power of the distance. Edser deduced this law, and I have applied it to calculate the observed physical properties of gases and liquids. The law is supposed to hold up to the instant of collision. Actually it represents the average effect of attractions and repulsions, which depend on the orientation of the particles. When the solid condition is approached, and particles become more or less fixed in their positions, the question of orientation becomes important. Then the simple eighth-power law may not hold. It should not be impossible to devise a law that would take account of both attraction and repulsion, and thus to extend the discussion to the solid state.

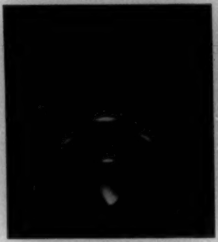


Figure 1. Surface scum on mercury pipetted from glass.

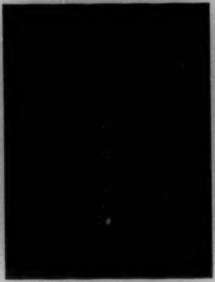


Figure 2. Thick surface skin on mercury.

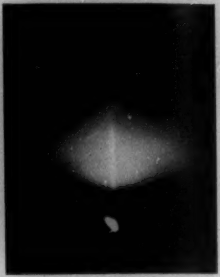


Figure 3. Thin surface skin on mercury.

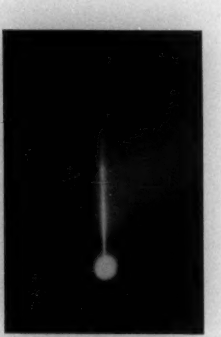


Figure 4. Surface skin of average thickness on mercury.

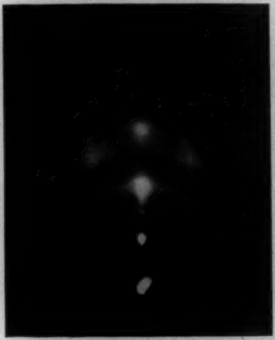


Figure 5. Gold evaporated on to a mercury surface skin.

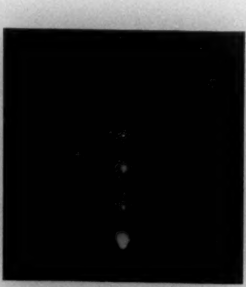


Figure 6. Gold amalgam formed on stirring.

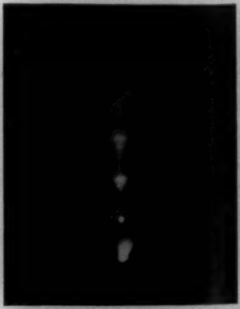


Figure 7. Mercuric bromide formed on a mercury surface.

To face page 63

THE SURFACE STRUCTURE OF LIQUID MERCURY

By G. L. J. BAILEY, S. FORDHAM and J. T. TYSON
Imperial College of Science and Technology

Received 5 *October* 1937. *Read* 12 *November* 1937

ABSTRACT. Previous workers have obtained by electron-diffraction from liquid-mercury surfaces either evidence of a crystalline structure, which they attributed to the mercury, or inconclusive results in that only incoherent scattering was observed. The present work explains these discrepancies and shows that liquid-mercury surfaces are in reality amorphous, but are generally covered with a thin crystalline film of some adventitious impurity.

---

§1. INTRODUCTION

Several workers⁽¹⁾ have shown by X-ray diffraction that the interior of a mass of liquid mercury is amorphous. On the other hand Wierl⁽²⁾, Kakesita⁽³⁾ and Berdennikov, Bresler, Zelmanov and Schtrauf⁽⁴⁾ obtained by electron-diffraction evidence of a crystalline surface structure which led them to suggest that the surface of the liquid was crystalline, the structure being either face-centred-cubic⁽²⁾, face-centred-rhombohedral⁽³⁾ or hexagonal⁽⁴⁾. Trillat⁽⁵⁾, Raether⁽⁶⁾ and Papsdorf⁽⁷⁾, however, also using electron-diffraction, could find no signs either of sharp rings or even of haloes in their patterns obtained from liquid mercury at grazing incidence, and it is unlikely that this could have been due merely to a preponderance of inelastic scattering of the electrons. Trillat seems to have used a very small mercury drop, and the varying refractive effects due to the correspondingly large curvature of the surface may well have caused sufficient blurring to obliterate the diffraction pattern. Raether and Papsdorf used flowing, and therefore presumably exceptionally clean, mercury surfaces from which the metal should have been able to evaporate freely and unhindered by any surface skin of impurity. Experience has shown, however, that it is impossible to obtain satisfactory electron-diffraction photographs in a camera saturated with mercury vapour at room-temperature; thus, according to kinetic theory, at a pressure of 10^{-3} mm., 85 per cent of the electrons would collide with mercury atoms after diffraction in a camera with an effective length of 43 cm. Schöbitz⁽⁸⁾ has in fact stated that the pressure in his apparatus had to be less than 10^{-5} mm. before clear diffraction patterns could be obtained. Thus it would seem experimentally impracticable to record the electron-diffraction pattern from a clean mercury surface.

In the experiments described below, the main object of which was to study the structure of the liquid mercury surface, quiescent mercury pools alone were used. Repeated attempts were made to eliminate all traces of surface impurity, but these were never entirely successful although in some cases the scum thickness was reduced to such an extent as to permit penetration by the electron beam down to the underlying mercury surface. Thin though such a skin must have been, it evidently sufficed greatly, if not indeed completely, to suppress the evaporation of mercury, because otherwise it is difficult to see how clear diffraction patterns could have been obtained.

§ 2. EXPERIMENTAL

The electron-diffraction camera used was similar to that described by Finch, Quarrell and Wilman$^{(9)}$ but was built for use in a horizontal position. The camera length was 43 cm., and the accelerating potential usually about 50 kv. The mercury was contained in an ebonite or iron cup, 3 cm. in diameter, filled brim-full, and previously cleaned with redistilled benzene. When the ebonite cup was used the mercury was earthed by means of a fine platinum wire. The nature of the container had no effect upon the results obtained.

The mercury was cleaned by repeated washing in 10-per-cent nitric acid solution and distillation in air at a few centimetres pressure, and gave a surface with an untarnished appearance. Nevertheless, after filtration into the cup through a dry filter-paper pierced with a small hole, or after transference by means of a clean glass pipette, a pattern, figure 1, was obtained consisting of short arcs and evidently due to an oriented surface impurity, since the spacings deduced from the pattern bore no relation to the known structure of mercury. The next surfaces were therefore prepared by sucking over into the apparatus under high vacuum, the mercury being withdrawn from well below its surface in an external vessel in order to leave behind the surface film. The patterns obtained from such surfaces varied from a series of sharp spots normal to the edge of the shadow of the specimen, figure 2, through all stages of resolution to a faint continuous streak corresponding to a film thickness of only a few layers of atoms, figure 3. When the streak was faint and practically continuous and the surface film therefore extremely thin, two faint haloes also were obtained, and these were undoubtedly due to the underlying mercury surface. Thus the halo-diameters agreed sufficiently well with those obtained by X rays from liquid mercury. For example, the second halo, which was the most suitable for measurement, gave a spacing of 1·3 ± 0·1 A. as compared with 1·4 A. obtained by X rays. It was not found possible to determine the nature of the adventitious polycrystalline surface film. The pattern was similar to a rotation photograph, and an orthorhombic structure could be assigned in which $a = 3{\cdot}40$ A., $b = 3{\cdot}92$ A., and $c = 6{\cdot}8$ A., the (100) planes being parallel to the surface. This does not agree with the known structure of mercuric oxide, nor did the film thicken on exposure to air; hence it seems that the film could not have been caused by surface oxidation. The spots observed by Raether$^{(6)}$ were probably due to the same substance, since the observed spacings are identical. The relative intensity of the halo pattern could be increased to a limited extent by heating the surface *in vacuo* by radiation from a white-hot tungsten filament.

The mercury surfaces used in the next experiments were covered with a surface film of such thinness that the row of spots normal to the shadow-edge was drawn out by refraction and lack of resolution into a continuous streak of varying width, figure 4. The effective length of the crystals normal to the mercury surface may be estimated as follows. With very thin crystals, the inner potential causes electrons that have been diffracted by true reflection to strike the photographic plate not at the region of normal maximum intensity, but somewhat nearer to the central spot. The Scherrer type of equation may, however, be applied to those parts of the diffraction which lie on the sides of the intensity maxima away from the undeflected beam, since these can be produced only by electrons which are diffracted by transmission. In this way the average thickness of the films on the mercury surfaces was estimated as 9 A. We have verified Scherrer's equation with patterns obtained from unimolecular films of hydrocarbons of known chain length; thus with a monolayer of dotriacontane, $C_{32}H_{66}$, which has a chain-length of 39 A., the half-width of the layer lines not deflected by inner potential gave a calculated length of 37 A. Similar film-thickness measurements with monolayers of other hydrocarbons down to $C_{22}H_{46}$ also gave results which sufficed to show that Scherrer's equation can be relied upon as a first approximation in the special case under consideration.

The wide differences in the patterns obtained from the surfaces of mercury render it unlikely that they were due to any surface crystallinity of the mercury itself. In order to obtain definite information on this point, films of readily amalgamated metals were evaporated on to such surfaces. Immediately after condensation from the vapour on to a still mercury surface, a pattern, figure 5, characteristic of gold in pronounced (111) orientation was obtained, and provided that any disturbance of the mercury surface was avoided the gold pattern remained unchanged, showing that the surface skin of unknown material acted as an effective barrier between the gold and the mercury and, indeed, must also have been effective in preventing escape of mercury vapour. After stirring with a glass rod, however, the gold pattern gave place to one characteristic of a face-centred-cubic structure in which $a = 5{\cdot}58$ A., figure 6. This structure differs from those of the gold amalgams previously studied by Aylmer, Finch and Fordham(10). Silver on evaporation gave initially a pattern of arcs due to a substance of unknown structure; when the surface was left standing, the arcs merely tended to lengthen into rings, but after agitation of the surface a pattern similar to that of the gold amalgam was obtained. Evaporated aluminium gave initially two haloes, but after the surface had been kept standing in air, a sharp ring pattern was obtained corresponding to a face-centred-cubic structure of side 3·74 A.; this does not correspond to any known structure of aluminium or of its oxide or hydroxides. Cobalt and chromium also gave very diffuse rings, but in these cases no change occurred on standing or agitation.

Further confirmation of the view that the arc and spot patterns were due to a surface impurity was obtained by the study of the action of ozone. This is known to oxidize agitated and therefore clean mercury surfaces to a slight extent at room-temperatures, although no visible reaction occurs with stationary surfaces. In our experiments, ozone at a concentration which amply sufficed to cause mercury to tail on glass or to blacken heated silver merely produced a slight reduction in the intensity of the initial streak, the halo pattern remaining unchanged. Therefore, apart from the unlikely event of the formation of a very thin protective film of an amorphous oxide, it must be concluded that the surface film, although only a few atom layers thick, afforded virtually complete protection of the mercury beneath from attack by the ozone.

The surface film could be broken by more energetic reagents, such as the halogens. These then attacked the mercury surface to form the orthorhombic mercuric halides in (010) orientation, the pattern, figure 7, of mercuric bromide being typical of those obtained in this manner; the *b* axis is here taken as that with a spacing intermediate between the shorter *a* and longer *c* axes. The iodide film was therefore probably the yellow mercuric iodide, but this could not be verified visually since the films were so thin as to show only first-order interference colours. In all the patterns the central row of spots was extended by refraction and lack of resolution to form a streak similar to that observed with the mercury surfaces themselves; the spacing of the spots was, however, characteristic of the halides and not of the surface impurity.

§ 3. DISCUSSION OF RESULTS

The photographs obtained from liquid-mercury surfaces may be resolved into two constituent diffraction diagrams. One, characteristic of a crystalline compound, must be due to a surface impurity for the following reasons. First, the diagram obtained varied from an arc pattern, when no great care was taken to obtain a very clean surface, to a streak normal to the plane of the liquid surface when special precautions aiming at the formation of a skin-free surface had been taken. Such a streak is characteristic of a very thin continuous film examined by reflection; similar diagrams can be obtained, for example, from slightly oxidized or corroded copper surfaces. Secondly, entirely different crystal structures have been obtained in the present work and by each of the three previous investigators, a fact which can be reasonably explained only by assuming the presence of an adventitious surface scum. Thirdly, ozone was found to have no effect on the mercury. Finally, experimental proof of the existence of the skin is afforded by the fact that gold evaporated on to the mercury surfaces was not attacked unless the mercury was agitated. This experiment is of particular interest in connexion with the work of Finch, Quarrell and Roebuck$^{(11)}$, who showed that the Beilby layer on certain polished metals is capable of dissolving other metals to a remarkable extent provided that the polished surface is free from a contaminating film of grease or oxide.

The second type of diffraction pattern, consisting of two haloes, was observed only when the surface film was extremely thin (less than about 10 A.) and was therefore due to the underlying mercury surface. This interpretation is supported by the fact that the halo-diameters were those to be expected from liquid mercury. The conclusion must therefore be drawn that, in contradiction to previous statements, the surface of liquid mercury is truly amorphous and has the same structure as that obtained for the interior by means of X-ray diffraction. As a general rule, however, a mercury surface is covered with a more or less thin crystalline skin of some adventitious impurity, even though special precautions may have been taken to prevent such a film from forming.

§4. ACKOWLEDGEMENTS

The authors thank Professor G. I. Finch for his unfailing interest and advice, and one of them (S. F.) wishes to thank the Department of Scientific and Industrial Research for a grant.

REFERENCES

(1) Debye, P. and Menke, H. *Phys. Z.* **31**, 797 (1930).
Prins, J. A. *Physica, Eindhoven*, **6**, 315 (1926).
Coster, D. and Prins, J. A. *J. Phys. Radium*, **9**, 153 (1928).
Wolf, M. *Z. Phys.* **53**, 72 (1929).
Menke, H. *Phys. Z.* **33**, 593 (1932).
(2) Wierl, R. *Verh. Dtsch. Phys. Ges.* **11**, 29 (1930).
(3) Kakesita, H. *Mem. Coll. Sci. Kyoto*, **17**, 241 (1934).
(4) Berdennikov, V. P., Bresler, S. E., Zelmanov, I. and Schtrauf, E. A. *J. Phys. Chem. U.S.S.R.* **5**, 584 (1934). *Brit. Chem. Abst.* p. 25 (1937).
(5) Trillat, J. J. *Trans. Faraday Soc.* **29**, 995 (1933).
(6) Raether, H. *Z. Phys.* **86**, 82 (1933).
(7) Papsdorf, W. *Ann. Phys., Lpz.*, **28**, 555 (1937). Cf. Kirchner, F. *Trans. Faraday Soc.* **31**, 1114 (1935).
(8) Schöbitz, E. *Phys. Z.* **32**, 37 (1931).
(9) Finch, G. I., Quarrell, A. G. and Wilman, H. *Trans. Faraday Soc.* **31**, 1051 (1935).
(10) Aylmer, A. E., Finch, G. I. and Fordham, S. *Trans. Faraday Soc.* **32**, 864 (1936).
(11) Finch, G. I., Quarrell, A. G. and Roebuck, J. S. *Proc. Roy. Soc.* A, **145**, 676 (1934).

DISCUSSION

Dr R. O. Jenkins: I have read this paper with interest, as it repeats results I obtained over three years ago, which may be found in my London University Ph.D. thesis. In my experiments I found that ordinary clean mercury gave a pattern similar to that in figure 3, consisting of the line which I attributed to a thin oriented oxide layer, and two diffuse haloes from the underlying mercury. By drawing freshly distilled mercury under vacuum into the apparatus and then using it to overflow the surface, it was found possible almost to eliminate the surface skin line, leaving only the haloes from the mercury itself. Their lattice spacings were 2·47 and 1·33 A. respectively, while X-ray work indicates values of 2·56 and 1·39 A. The slight discrepancy is possibly due to atoms being more closely packed near the surface as a result of the atomic forces on them being asymmetrical, the net effect being to pull the surface atoms into the liquid.

The authors have however made an important omission in failing to discuss the possibility of refraction in their interpretation of the two diffuse haloes. If the surface is electron-optically flat, the haloes will be displaced from their true positions. It can be shown that if the inner potential has the likely value of about 15 V., the second halo when refracted will be where the first one was, and a possible third halo will take the place of the second to within close limits. Owing to the diffuseness of the haloes, this effect would not be observed. It is possible however by varying the angle of incidence of the electron beam on the mercury surface to alter the radius of the outer halo by about 12 per cent if it is a refracted halo. This change however could not be detected in practice, and it seems probable that the haloes were not refracted and that the mercury surface was therefore not electron-optically flat.

Dr H. CHATLEY: Will the authors define "amorphous"?

Dr O. KANTOROWICZ: As to the meaning of the terms amorphous and crystalline, I would like to draw attention to a paper by B. E. Warren in the October issue (1937) of the *Journal of applied Physics*, in which he discusses this problem in respect of fused silica. He states that if one tentatively assumes fused silica to be composed of minute crystals of cristobalite and estimates their size by Bragg's formula from the broadening of Debye-Scherrer rings, the average size of the assumed crystals is found to be 7·7 A. On the other hand the length of a unit cell of cristobalite is 7·0 A. It follows that the assumed crystals on the average do not contain more than one unit cell, and that there is no indication of an extended lattice. Dr Warren concludes that there is no sense in debating whether fused silica is amorphous or composed of small crystals, for these crystals, if they exist, must be so small that the arrangement of atoms would not be different from that in an amorphous mass. I entirely agree.

The authors say that no difference can be established by their method if their crystal-size is as small as 15 A. That is not surprising. Let us assume an even bigger crystal of cubic form and containing 1000 atoms. One realizes at once that of these, 488 are situated on the very surface of the crystal. That means that for about half the atoms the distances to about 20 per cent of their nearest neighbours (e.g. those in the neighbouring crystal) are not determined by the laws that govern the regular spacing inside the crystal. Consequently all methods that are based on the interference of wave trains originating from evenly spaced atoms will give disturbed results, the degree of disturbance increasing with decrease in particle-size as more and more atoms find themselves on the surface. (For instance the disturbance is 80 per cent for 5^3 or 125 atoms.)

As the sensitivity of different experimental methods as to the misarrangement of atoms might be different, one and the same body might with one method indicate an amorphous, random distribution of atoms, and with another method a crystalline lattice. On the other hand, for each method there will be a maximum particle-size below which the distinction between crystalline and amorphous states becomes inapplicable in principle. In this range any discussion as to the state of the body must be fruitless. I therefore submit the terms "amorphous" and "crystalline" should be used in relation to the method of investigation only.

Reply by Dr FORDHAM: I am interested to hear that Dr Jenkins has obtained experimental results similar to ours, although as a result of our experience, and not having seen Dr Jenkins's photographs, I am still somewhat dubious as to the possibility of obtaining satisfactory electron-diffraction photographs from a perfectly clean mercury surface. Like Dr Jenkins, we could find no evidence of refraction and therefore did not discuss its possible effects. A similar lack of refraction has been noted by French in the case of the Beilby layer. Owing to the large angles of incidence employed in our experiments, the maximum change introduced in the diameter of the second halo by an inner potential of 15 v. would only have been about 10 per cent. Such refraction would have caused appreciable lack of circularity about the central spot, but no such eccentricity was ever observed. These considerations, of course, have little or no bearing on the determination of the structure of the liquid mercury surface, although they may indicate, as Dr Jenkins suggests, that liquid mercury surfaces are not electron-optically flat.

In reply to Dr Chatley; I should call "crystalline" any substance in which the constituent atoms are arranged regularly for at least two unit translations in all directions, and also larger two-dimensional networks. All other substances I should call "amorphous". The difficulty of definition arises from the fact that the terms "amorphous" and "crystalline" are not mutually exclusive, but refer merely to two extreme types of large-scale structures.

Thus, whilst agreeing in the main with the remarks of Dr Kantorowicz, I prefer a definition of "amorphous" which is independent of experimental method and which embodies only the general conception of crystallinity as regular repetition in all directions. Dr Kantorowicz seems to overestimate the importance of intercrystalline scattering; the nature of the interference function is really such that even with a bimolecular liquid the positions of the maxima are determined largely by the intermolecular spacing. Since, however, crystalline spacings are in general not very different from the closest distance of approach of atoms in the corresponding monatomic liquid, it cannot be said that the X-ray or electron-diffraction results rule out the possibility of a small degree of association in liquid mercury, but our results do show that the surface has fundamentally the same structure as the interior of the liquid, and that the large-scale crystallinity reported by previous workers was due to films of impurity.

VIBRATIONS OF FREE CIRCULAR PLATES. PART 1: NORMAL MODES

By MARY D. WALLER, B.Sc., F.Inst.P., Lecturer in Physics, London (Royal Free Hospital) School of Medicine for Women

Received 15 *October* 1937. *Read* 26 *November* 1937

ABSTRACT. The normal vibrating modes of free circular plates have been determined over an interval of more than six octaves, the solid-carbon-dioxide method of excitation being used to produce the nodal figures, and a valve oscillator to measure their frequencies. It is concluded that the nodal system of ideally uniform and entirely free plates would, in accordance with theory, consist only of circles, diameters and combinations of circles and diameters. It is found that although each simple mode has its characteristic frequency, cases occur in which the difference between two or even three of these is very small, and the number of nodal diameters, which as regards raising the pitch are approximately equivalent to one nodal circle, increases from two to five, in the interval investigated, in passing from figures with relatively more circles to those with relatively more diameters. The expression, based on approximate theory, for calculating the frequencies of the higher modes, in which it is assumed that the addition of two nodal diameters increases the frequency by as much as one nodal circle, is accordingly not applicable in ordinary practice.

It is suggested that the simple and rapid solid-carbon-dioxide method of exciting free vibrations might be employed for testing the uniformity of plates, for detecting internal flaws, for studying recrystallization phenomena, and for obtaining comparative values of Poisson's ratio of metals and alloys.

§ 1. INTRODUCTION

THE main facts regarding the vibrations of free circular plates, both theoretical and practical, are given in Rayleigh's treatise on *Sound*, vol. **1**, chapter 10 (§§ 218–23). The critical discussions and suggestions made not only in this chapter, but also in the preceding one which deals with vibrating membranes, have been much used in connexion with the present work.

The nodal figures of free circular plates, as also those of any other system of revolution, should, according to theory, consist of diameters symmetrically distributed round the centre, but otherwise arbitrary, together with concentric circles. In practice, however, it is well known that many other designs are frequently produced, which have never been systematically studied or adequately explained. The solid-carbon-dioxide method of producing vibrations⁽¹⁾ possesses peculiar advantages for doing this since vibration frequencies other than those natural to the plate cannot be produced and the excitation can be made on any part of the surface. It appears that the most extensive list of observed normal vibration frequencies of free circular plates is still that of Chladni⁽²⁾. His results are given in the notation of the chromatic scale, and in view of the apparatus at his disposal they are necessarily

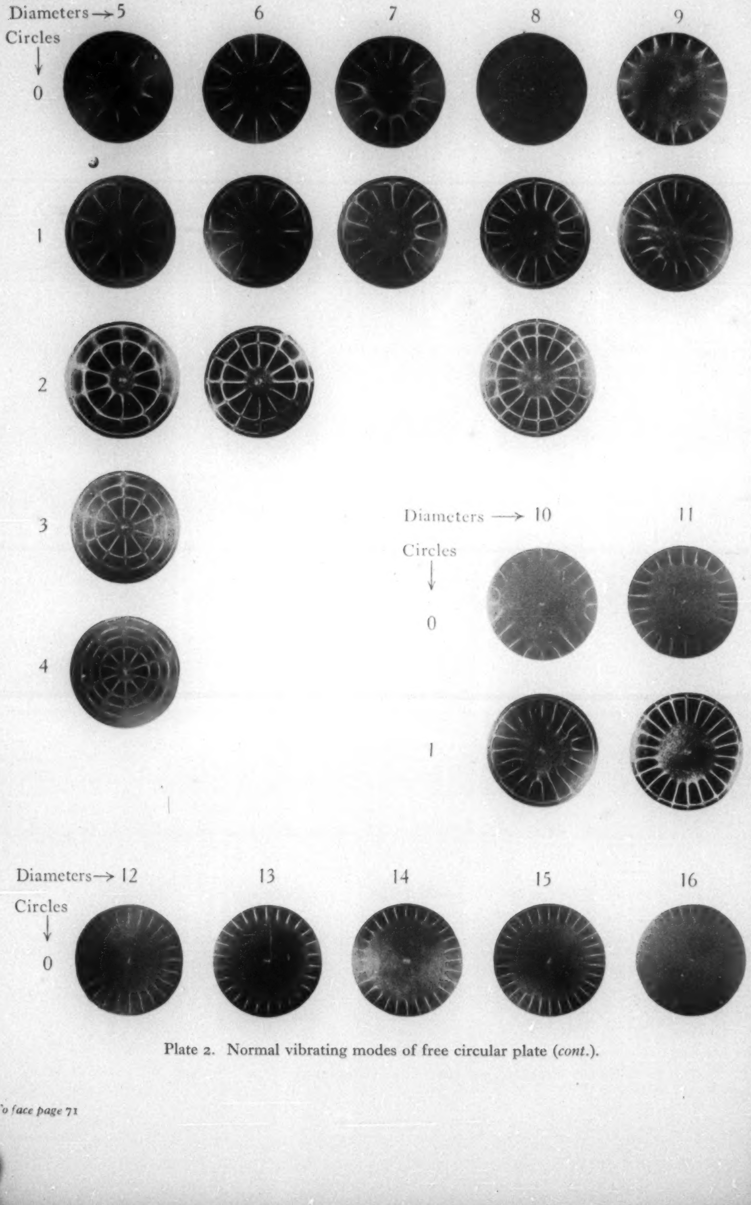

Diameters → 5
6
7
8
9
Circles ↓
0
1
2
3
4
Diameters → 10
11
Circles ↓
0
1
Diameters → 12
13
14
15
16
Circles ↓
0

Plate 2. Normal vibrating modes of free circular plate (*cont.*).

only approximate. They do not extend far enough to explain the greater number of his own nodal patterns nor those produced during the present investigation. Strehlke's⁽³⁾ measurements of the radii of nodal circles will be referred to in due course.

Kirchhoff's theoretical frequencies, which on account of the lengthy calculations involved are restricted to the graver tones, will be considered later, and it will then be shown that the approximate expression for calculating the higher partials is not generally applicable in practice.

The present part of the paper describes and discusses the observations that have been made to obtain the frequencies and nodal systems of the normal vibrating modes over an interval of about six octaves. Part 2 will be concerned with a large number of nodal designs, other than those consisting of circles and diameters. As a result of these studies it has been found possible to interpret Chladni's original figures on circular plates, and these are considered in part 3.

§ 2. EXPERIMENTAL ARRANGEMENTS

Frequencies. The frequencies of the vibrations were determined by the method of beats by means of a mains operated calibrated valve oscillator.

Plates. A considerable number of plates of different sizes were employed, but final measurements were restricted as far as possible to large and thin plates. The diameters of two of these, for example, were 30·47 and 25·71 cm. respectively, the thickness in each case being approximately 2 mm. The importance of using thin plates is emphasized by some recent work of A. B. Wood(4) in which he shows how the frequencies of the two gravest tones of free circular plates gradually diminish as the ratio of thickness to diameter increases.

Supports and manner of excitation. When figures with a central node were obtained, the plates were supported centrally in the usual manner. The diameter of the hole in the plate was 5 mm. In order to obtain the nodal circles, the plate under test (preferably one without a central hole) was laid on three equidistant small circular-sectioned pieces of indiarubber, which were placed in appropriate nodal positions on a horizontal table provided with a paper scale graduated in circles and angles. With the first arrangement of support, the solid carbon dioxide was usually applied to the under surface of the plate, and with the second arrangement to the upper surface. A second translucent graduated scale, which could be laid on the surface of the plate, was often found useful in deciding on the point of excitation. While the surface was being sprinkled with sand this position was protected by means of a small proof plane which was afterwards removed. A desired nodal figure was also sometimes encouraged by gently touching the plate at one or two appropriate nodal positions by means of a divider. In order to obtain the best figures the experiments were made on dry days(1), dried sand being sprinkled just before the excitation on polished plates from which any grease had been removed with xylol. The Drikold solid carbon dioxide used for exciting the plates was very kindly given by Imperial Chemical Industries Ltd.

Photographs. Since it was desirable, for purposes of comparison, that all nodal figures should be given on the same scale, some of the photographs shown in the plates are enlargements of the original photographs. The two to eight diameter-only figures, obtained in the first instance on small vibrating plates by means of solid carbon dioxide, have been replaced by figures produced by bowing on the larger vibrating plates.

Radii of nodal circles. The radii of the nodal circles were measured directly on the vibrating plates and the results confirmed subsequently on the photographs, either a travelling microscope or a projection lantern being used.

§ 3. EXPERIMENTAL RESULTS

The nodal systems extending over an interval of nearly six octaves are shown in plates 1 and 2, in which each column contains figures with a given number of nodal diameters and each row figures with a constant number of nodal circles. In most of the figures, the small want of uniformity in thickness which is generally present in large metal plates cannot be detected, but in the symmetrical figures of the first column a variation in thickness which was found to be less than 1 per cent has been sufficient to cause a considerable distortion in the innermost circles of the 4/0, 5/0 and 6/0 figures. The longer diameter corresponds with the direction of smaller thickness. At the 0/10 figure there is a very significant break in the regularity of the diameter figures of the first row. It was subsequently found possible to obtain figures without this irregularity on some particularly uniform steel plates kindly lent to me by Professor Andrade.

For the frequencies of the vibrations the various nodal systems are expressed as multiples of the gravest, 0/2 mode (i.e. the mode characterized by 0 circles and 2 diameters), and are given in table 1. It will be seen that although each frequency is

Table 1. Relative frequencies of normal vibrating modes of free circular brass plate

Diameters Circles	0	1	2	3	4	5	6	7	8	9	10	11	12
0			1*	2·29	4·10	6·19	8·80	11·7	15·1	18·8	23·0	27·6	33·0
1	1·70	3·99	6·79	10·3	13·8	18·1	23·1	28·6	34·7	40·8	47·5	54·7	63·0
2	7·51	11·7	16·1	21·2	27·1	33·4	40·5	47·7	56·0	*65*	*75*	*86*	*100*
3	16·4	22·7	29·4	36·3	43·0	50·5	59	*69*	*80*	*90*	*(104)*	*(118)*	*(135)*
4	29·1	37·0	43·2	53·1	63·0	*74*	*86*	99	*(120)*	*(145)*			
5	47·0	56·0	*66*	*77*	*92*	*(110)*	*(135)*						
6	72·7	*83*	*100*	*(127)*	*(147)*								
7	(110)	*(132)*	*(160)*										

Diameters Circles	13	14	15	16	17	18	19	20	21	22	23	24
0	38·0	44·5	51·0	58·0	65·5	74·3	83·5	90·9	100	109	118	127
1	*72·5*	(81)	(90)	*(97)*	*(108)*	*(120)*	*(135)*					
2	*(115)*											

The figures in italics are approximate and those in brackets have been estimated by extrapolation only or by rough measurements on a large plate 46·7 cm. in diameter.

* Actual frequencies of the plates 30·47 and 25·7 cm. in diameter were 80·9 and 113·3 c./sec. respectively.

distinct, cases occur in which there is very little difference between two or even three of the numbers. In particular the 0/10 relative frequency, 23·0, is very near to that of the 1/6 mode, 23·1. It becomes evident, then, that the imperfect 0/10 nodal figure is due to the double circumstance of a departure from perfect symmetry in the plate and a near coincidence of natural periods. We shall return to this important result in part 2. Other small irregularities will also then receive an adequate explanation.

Table 1 also includes some further frequencies which have been obtained either by extrapolation or from recent observations which have been made without photographing the nodal systems. Some of the approximate numbers of the highest partials are in italics; they will be needed in parts 2 and 3. Measurements of the radii of the nodal circles, given relatively to the plate's radius, are shown in table 2.

Table 2. Radii of nodal circles relative to that of the disc, taken as 1000

Diameters Circles	0	1	2	3	4	5	6	7	8	9	10	11
1	680	781	823	843	859	871	880	889	897	903	909	912
2	391	497	562	604	635	662	681	702	715			
	843	867	887	898	906	915	922	927	932			
3	257	349	415	461	505	531						
	591	643	681	706	728	745						
	895	902	913	919	925	933						
4	190	269	328	374	411	443						
	441	495	540	571	596	623						
	692	726	748	764	779	794						
	918	928	934	938	941	944						
5	154											
	351											
	548											
	753											
	956											
6	131											
	292											
	456											
	624											
	794											
	958											

§4. COMPARISON WITH PREVIOUS RESULTS AND WITH THEORY

Chladni's law. It is evident from table 1 (see also the last column of table 1, part 2) that Chladni's experimental conclusion(a), which states that the addition of 2 nodal diameters raises the pitch by approximately the same amount as that of 1 nodal circle, has not been substantiated. This number increases from 2 to 5 in the interval investigated, being least for the vibrating modes shown on the lower left-hand side and greatest for those shown on the upper right-hand side of the table. Since the approximate expression (see below) for calculating the frequencies of higher partials also makes the assumption made by Chladni, it has been necessary to examine the evidence very carefully.

A study of Chladni's work⁽²⁾ shows that he was more interested in producing nodal circles than in producing nodal diameters, and that whenever possible he supported and controlled his plates by hand. His table of frequencies extends only to 8 nodal diameters, but as far as 6 nodal circles which characterize roughly the same pitch as 18 diameters. It appears that he must have formulated his law with reference to the frequencies at the lower left hand of table 1 of the present paper. This is all the more curious since his own table gives evidence of three diameters being equivalent to one circle. For example the pitch g' is given both for figure 0/5 and for 1/2, b'' for 0/8 and 2/2, and g''' for 1/7 and 2/4. His nodal figures, which are the subject of part 3, also provide much evidence of more than two diameters being equivalent to one circle.

According to the approximate expression⁽³⁾ for calculating the higher roots of Kirchhoff's free-plate equation the frequencies of the normal vibrating modes are proportional to $(n+2h)^2$, where n is the number of diameters and h is an integer. It will be best to quote Rayleigh's own words, in which the expression in question is quoted as (4)*: "It appears by a numerical comparison that h is identical with the number of circular nodes.... *Within the limits of application of* (4), we see also that the pitch is approximately unaltered, when any number is subtracted from h, provided twice that number be added to n. This law, of which *traces* appear in the following table, may be expressed by saying that towards raising the pitch nodal circles have twice the effect of nodal diameters. It is probable that, strictly speaking, *no two components have exactly the same pitch*."

It appears from the present observations, that Chladni's law applies to very few of the partials in the first six octaves. When it is remembered that Kirchhoff's theory was formulated for thin plates and how the nodal diameters crowd up to the centre of the plate it is scarcely to be expected that any constant relation will exist between the number of nodal diameters and nodal circles which must be added in order to raise the vibration frequency by the same amount.

Before leaving this subject it is interesting to note that A. B. Wood⁽⁴⁾ found a tendency for his 1/0 observations to yield somewhat higher values of velocity of sound than those derived from 0/1 observations.

Poisson's ratio. In the case of transversely vibrating plates, both Poisson's ratio and Young's modulus are factors determining the frequency of vibration, which, other conditions being constant, should vary with the material of the plate.

Since Chladni preferred glass to metal plates, it may fairly be assumed that his observations correspond to a value of Poisson's ratio σ such that $\sigma \doteqdot \frac{1}{4}$. A few vibration frequencies obtained with plates made of brass, for which $\sigma \doteqdot \frac{1}{3}$, and steel, for which $\sigma \doteqdot \frac{1}{4}$, are compared with Chladni's results in table 3, in which also some calculated frequencies due to Kirchhoff⁽³⁾ for values $\frac{1}{3}$ and $\frac{1}{4}$ of σ are included.

It will be seen that an alteration of σ from 1/4 to 1/3 produces nearly a 7 per cent increase in the relative frequency of the 1/1 mode. These results are sufficiently striking to make further observations on plates of identical dimensions but of varying

---

* The italics are mine, and the table to which he refers extends only as far as 2 circles and 3 diameters.

Table 3. Comparison of results. Frequencies relative to that of the gravest mode, 0/2

Circles	Diameters	Material of plate. Observed relative frequencies			Kirchhoff's calculation (3)	
		Brass $\sigma \doteqdot \frac{1}{3}$	Steel $\sigma \doteqdot \frac{1}{4}$	Chladni glass* $\sigma \doteqdot \frac{1}{4}$	$\sigma = \frac{1}{3}$	$\sigma = \frac{1}{4}$
1	0	1·7	—	1·60	1·73	1·61
1	1	3·99	3·77 3·82	3·75	3·91	3·70
0	4	4·10	4·12 4·03	4·0	4·05	—

* The measurements were almost certainly made on glass plates (2).

material desirable. Table 4 may also be examined in connexion with this subject. In it Strehlke's (3) measurements on glass plates have been compared with the present measurements made on brass plates and with Kirchhoff's calculated values for $\sigma = \frac{1}{3}$ and $\frac{1}{4}$ respectively. It is perhaps just possible to detect the influence of Poisson's ratio in the later figures.

Table 4. Comparison of results. Radii of circular nodes (radius of disc = 1000)

Circles	Diameters	Observed on brass $\sigma \doteqdot \frac{1}{3}$	Strehlke Observed on glass $\sigma \doteqdot \frac{1}{4}$	From Kirchhoff's theory	
				$\sigma = \frac{1}{3}$	$\sigma = \frac{1}{4}$
1	0	680	678	—	681
2	0	391	391	—	391
		843	841	—	842
3	0	257	256	—	257
		591	591	—	591
		895	894	—	894
1	1	781	782	780·8	781·4
1	2	823	810	822·7	821·9
1	3	843	840	846·8	845·2
2	1	497	490	497·1	497·7
		867	869	870·1	870·6

Measurements made on Chladni's drawings are not included since the results are variable.

§ 5. CONCLUSIONS

(1) By means of the solid-carbon-dioxide method of producing vibrations in metal objects it has been possible to obtain all the normal vibrating modes of free circular plates which occur in an interval of over six octaves.

(2) The nodal system of ideally uniform and perfectly free circular plates would consist, in agreement with theory, only of circles, diameters, or combinations of circles and diameters.

(3) The vibration frequencies of the normal vibrating modes are all distinct. Occasionally the frequencies of two or even three modes are very nearly equal.

(4) The number of nodal diameters which must be added to raise the frequency by as much as one nodal circle is not constant, but increases from two to five in the interval investigated. This increase occurs in passing from figures with relatively more circles to those with relatively more diameters. Approximate expressions for calculating the higher partials, which assume that this number is always equal to two, are accordingly inapplicable in practice.

(5) The relative frequencies of the overtones are appreciably affected by the value of Poisson's ratio in a manner which is in general agreement with theory.

§ 6. SUGGESTED APPLICATIONS

The following are some possible future applications of the solid-carbon-dioxide method of producing vibrations:

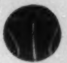
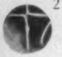
(1) *Rapid tests of uniformity of metal plates and detection of flaws.* Any departure from symmetry of a circular plate is at once apparent in the innermost nodal circle of the symmetrical nodal figures and this provides a sensitive method of detecting want of uniformity in plates. In this connexion it may be mentioned that a magnetostriction oscillator has recently been employed by Hayes(5) for the detection and location of laminations in steel plates.

(2) *Study of recrystallization phenomena.* It would be interesting to study alterations in the nodal figures, more especially perhaps in nodal circles, which would occur when a metal plate which had been rolled in one direction only was heated until recrystallization occurred. This subject has already been studied by Tammann and his collaborators(6, 7) principally on the two-diameter and three-diameter nodal figures produced by bowing.

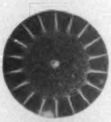
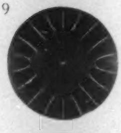
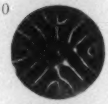
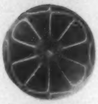
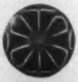
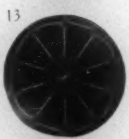
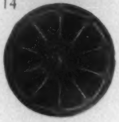
(3) *Comparative measurements of Poisson's ratio of metals and alloys.* It has been shown in table 3 that an alteration in the value of Poisson's ratio has an appreciable effect on the relative frequencies of the normal vibrating modes, which is possibly sufficient to provide a simple means of obtaining comparative values of Poisson's ratio for different metals.

REFERENCES

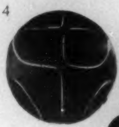
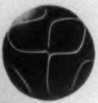
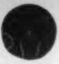
(1) WALLER, M. D. *Proc. Phys. Soc.* **49**, 522 (1937).
(2) CHLADNI. *Die Akustik*, §§ 134–41 (1802 or 1830).
(3) RAYLEIGH. *Theory of Sound*, **1**, 2nd ed. ch. 10, §§ 218–23 (1894).
(4) WOOD, A. B. *Proc. Phys. Soc.* **47**, 794 (1935).
(5) HAYES, H. C. *J. Acoust. Soc. Amer.* **8**, 220 (1937).
(6) SCHRÖDER, E. and TAMMANN, G. *Z. Metallk.* **16**, 200 (1924).
(7) TAMMANN, G. and RIEDELSBERGER, W. *Z. Metallk.* **18**, 105 and 149 (1926).

1

2

3

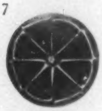
0/4, 1/1

8

9

10

11

12

13

14


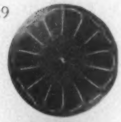
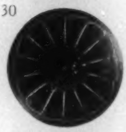
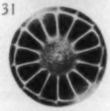
0/9, 1/5

4

5

6


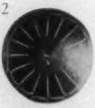
0/5, 1/2

7


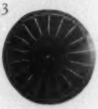
0/8, 1/4

29

30

31


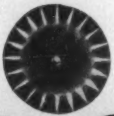
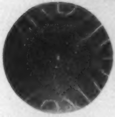
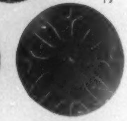
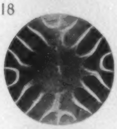
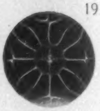
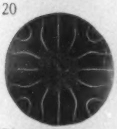
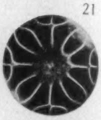
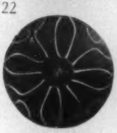
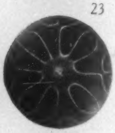
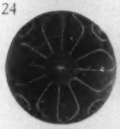
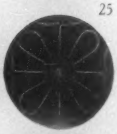
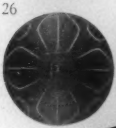
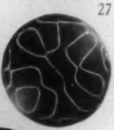
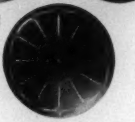
0/11, 1/7

32


0/12, 1/8

33


0/13, 1/9

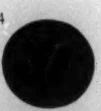
15

16

17

18

19

20

21

22

23

24

25

26

27

28


0/10, 1/6

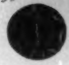
0 10 20
cm.

Combination of two vibrating modes.

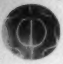
34



35

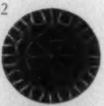


36

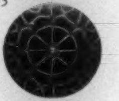


0/7, 2/1

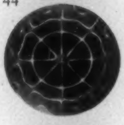
42



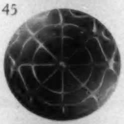
43



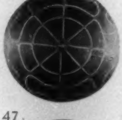
44



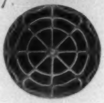
45



46

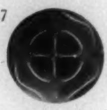


47



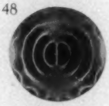
0/14, 3/4

37



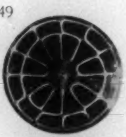
0/8, 2/2

48

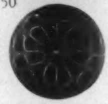


0/13, 4/1

49

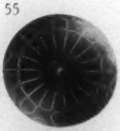


50

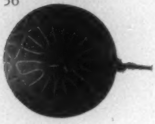


1/9, 2/6

55

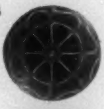


56

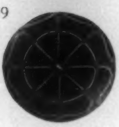


0/17, 1/12, 2/9

38

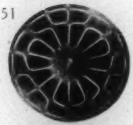


39

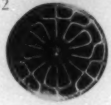


0/11, 2/4

51

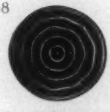


52



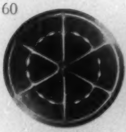
1/10, 2/7

58

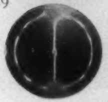


1/10, 2/7, 5/0

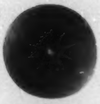
60



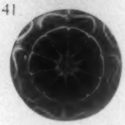
59



40

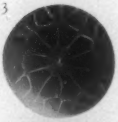


41

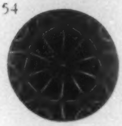


0/12, 2/5

53

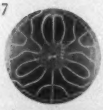


54



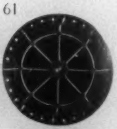
0/12, 1/8, 2/5

57

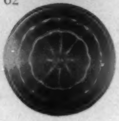


1/10, 2/7, 3/5

61



62



S

0 10 20
cm.

Compounded normal modes of vibration.

VIBRATIONS OF FREE CIRCULAR PLATES. PART 2: COMPOUNDED NORMAL MODES

By MARY D. WALLER, B.Sc., F.Inst.P., Lecturer in Physics, London (Royal Free Hospital) School of Medicine for Women

Received 15 *October* 1937. *Read* 26 *November* 1937

ABSTRACT. The many nodal designs (other than those consisting solely of circles and diameters) which are obtained on free circular plates are shown to consist of two or more compounded normal modes of vibration, the periods of which are very nearly equal. The vibration frequencies corresponding to the designs are intermediate between those of the combining modes. The figures are produced as a result of the slight divergence of free periods which exists in all but ideally uniform plates. An increase in damping, either internal or arising from the manner of support or of excitation, also favours the production of these designs, since it renders the resonance less sharp. Compounded modes of a somewhat similar character may be expected to occur in other systems of revolution, such as circular plates clamped at the edge, circular membranes, rings and cymbals, in all of which the normal nodal system consists of combinations of circles and diameters.

§ 1. INTRODUCTION

One of the earliest nodal designs produced by means of solid carbon dioxide was that shown in figure 21 of the present paper. It was noticed that whereas 12 nodal lines can be counted at the centre, there are 20 round the circumference. The figure appears to be a variant of either a 0/10 (no circles, ten diameters) figure or of a 1/6 (one circle, six diameters) figure, or really a combination of these two simple figures. This conclusion, arrived at visually, was subsequently confirmed by aural means when it was found that the vibration frequencies of the two simple modes of the compounded mode were practically identical.

This early observation supplied the key to the explanation of all the other figures that have been produced. The grouping of these figures is shown in the two plates; it was not completed until the knowledge regarding the normal vibrating modes which has been described in part 1 was available.

The combination of two simple modes is made possible by a slight want of uniformity in the plate under observation. Thus in the present experiments the thickness of the 30·47-cm.-diameter plate was found to vary from 2·040 to 2·020 mm. and that of the 25·71-cm.-diameter plate from 2·017 to 2·030 mm. This departure from exact symmetry causes a divergence of free periods (1a) and renders determinate the positions of the nodal diameters. The nodal figure will therefore vary according to the position of excitation, and it will be possible for two or more normal modes of neighbouring periods to coexist in any proportions. This compounding of modes may be compared with that which is always possible in the case of square plates(1b) where two fundamental modes, at least, have equal periods.

§ 2. TECHNIQUE

The plates were treated in the manner described in part 1, § 2. Both the bowing and the solid-carbon-dioxide methods of producing vibrations were used, the former for exciting at the edge, and the latter for exciting at other points on the surface of the plate. The figures shown at 1, 2, 4–6, 9, 17, 20, 23, 24, 27, 34–36, 48 and 55–58 in plates 1 and 2 were produced by bowing.

§ 3. COMPOUNDED NORMAL MODES

The groups of figures, arranged as far as possible in ascending order of tone, are shown in the two plates, and a summary of results is given in table 1.

Table 1. Compounded normal modes of vibration, figures 1 to 58

		Frequencies relative to 0/2 tone = 1	R*
Plate 1:	Two modes		
Figures 1 to 3	0/4, 1/1	4·10, 3·99	3
4 to 6	0/5, 1/2	6·19, 6·79	3
7	0/8, 1/4	15·1, 13·8	4
8 to 14	0/9, 1/5	18·8, 18·1	4
15 to 28	0/10, 1/6	23·0, 23·1	4
29 to 31	0/11, 1/7	27·6, 28·6	4
32	0/12, 1/8	33·0, 34·7	4
33	0/13, 1/9	38·0, 40·0	4
—	0/17, 1/12	65·5, 63·0	5
Plate 2:			
Figures 34 to 36	0/7, 2/1	11·7, 11·74	3
37	0/8, 2/2	15·1, 16·1	3
38, 39	0/11, 2/4	27·6, 27·1	3·5
40, 41	0/12, 2/5	33·0, 33·4	3·5
—	0/16, 2/8	58·0, 56·0	4
42 to 47	0/14, 3/4	44·5, 43·0	3·3
48	0/13, 4/1	38·0, 37·0	3
49, 50	1/9, 2/6	40·8, 40·5	3
51, 52	1/10, 2/7	47·5, 47·7	3
	Three modes		
53, 54	0/12, 1/8, 2/5	33·0, 34·7, 33·4	4, 3
55, 56	0/17, 1/12, 2/9	65·5, 63·0, 65·0	5, 3
57	1/10, 2/7, 3/5	47·5, 47·7, 50·5	3, 2
58	1/10, 2/7, 5/0	47·5, 47·7, 47·0	3, 2·3

* Number of nodal diameters which raise the pitch by approximately the same amount as one nodal circle.

The 0/10, 1/6 group (figures 15–28), of which figure 21 has already been mentioned, will first be considered in some detail.

It will be seen that the two simple modes, 0/10 (obtained on Prof. Andrade's uniform plate mentioned in part 1) and 1/6, are shown in figures 15 and 28 respectively. Between these figures there are two columns of compounded nodal figures in which it is interesting to compare the two different developments of design. The distorting effect of an additional clamp at the edge is shown in figure 27, which is only just recognizable as belonging to the group.

For the recognition of the basic normal modes of more complicated figures, it will be useful to record from observations made on this group that (1) A hoop at the circumference, figure 20, is an indication of 2 diameters in one of the constituent normal modes and of a circle in the other. (2) A loop from the centre, figure 25, indicates 2 diameters and 1 circle of one of the modes. (3) A bend in a nodal radius, figure 22, is evidence of the presence of a nodal circle in one of the modes.

Passing now to the other figures shown in plates 1 and 2, it may be remarked that the crown-like figure 3 (0/4, 1/1) is frequently obtained when a small plate is held at a node between the thumb and first finger and the solid carbon dioxide is applied in the middle of one of the two vibrating central portions; the plate is not quite free, and both this figure and figure 2 may be compared to the inverted Chladni figure 101*b*, part 3. An eccentric circular clamp was used in the production of figure 1. Figures 4 to 6, in the 0/5, 1/2 group, are again typical of plates which are unsupported so as to allow of entirely free vibration. The first two, if inverted, may be compared with Chladni's figure 102*b*. The component modes of figures 8 to 14 (in the 0/9, 1/5 group) are easily recognized, but the flatness of the hoop in figure 13 should be noted as this makes it easy to recognize the 0/8, 1/4, figure 7, and the component parts of several other nodal patterns.

The varying designs in the 0/14, 3/4 group, figures 42 to 47, may be noted, and especially the meaning of such wavy lines as are found in the last two figures, some of which indicate 3 and some 4 diameters. It is then possible to recognize the component modes of figures 37 and 38 or 39. Figure 48 (characterized as 0/13, 4/1) is the most important nodal design in connexion with the study of Chladni's own drawings, part 3, and shows the *Biegungen* or bendings which are so characteristic of many of them. Comparison with figures 36, 45, 44, 43 and 42 shows that each bending from crest to crest indicates two radii of one of the combining modes. Figure 58 should also be studied in this connexion; the waviness of the lines is typical of bow-excitation, and from them traces of the 1/10 and 2/7 modes can be recognized superposed on the predominating 5/0 mode. Three simple modes are combined in figure 54, of which 2/5 can be recognized by looking at the central portion of the plate 0/12 and by looking at the circumference, while the presence of 1/8 is seen by omitting diameters (indicated by 4 hoops at the circumference) and adding a circle in their place. The plate was clamped as in figure 56 (0/17, 1/12, 2/9), and excited by bowing. The double bend of some of the radii in figure 57 (1/10, 2/7, 3/5), indicative of two circles, may be noted; it is also possible to see a trace of the 3/5 mode in this nodal design.

The above conclusions regarding the combination of simple modes, which have been arrived at mainly by inspection of the nodal systems, are confirmed by finding that the vibration frequencies of the designs belonging to any one group are intermediate between the two nearly equal frequencies of the parent modes. The summary of results which is given in table 1 includes also several later observations on higher compound nodal designs which were not photographed. The numbers in the last column give the number of nodal diameters which raise the frequency of vibration by as much as does one nodal circle, and are of importance in connexion with the argument set out in § 4 of part 1.

Superposed sand figures. The four figures, 59 to 62, shown at the bottom of the right-hand side of plate 2, differ in character from those already considered, and were obtained by chance when it happened that the plate was excited a second time by means of solid carbon dioxide in such a way as to produce a second sand pattern, which because of its geometrical similarity did not disturb much of the first pattern. Figure 59 appears to be a 0/6 nodal pattern superposed on a 1/1 pattern, and figure 60 a 1/9 pattern superposed on a 2/3 pattern. Figure 61 is 0/9 superposed on 2/4, assuming the amplitude of the second vibration to have been insufficient to disturb the sand of the inner circle. Figure 62 is possibly made up of 0/9 with a compound vibration 1/10, 3/4 superposed on it. The vibration frequencies (which are unequal) of the two patterns do not of course enter into the elucidation of such figures.

§ 4. FURTHER REMARKS

Comparison with nodal designs of damped and forced vibrations. It is interesting to compare the present results with a large number of drawings made by Elsas⁽²⁾ showing the nodal figures obtained on damped circular membranes, the vibrations of which were forced. In such a case, as was shown subsequently by Debye⁽³⁾, it is possible for two neighbouring natural modes to combine because of the flatness of resonance. In fact a simple mode is never produced singly. Franke⁽⁴⁾ has followed up this work with a study of the forced vibrations of clamped circular plates, and a paper by Shünemann⁽⁵⁾ may also be mentioned in this connexion. Though the figures are of course not the same as those given by free circular plates, yet since they are also those of a system of revolution they often bear a strong resemblance to some of them. There is, I think, evidence of forcing or at any rate external damping in many of the figures obtained by Colwell⁽⁶⁾ on free circular plates by means of a magnetostriction oscillator. The exciter has its own period, and a very nice adjustment of frequency is necessary in order to avoid an element of forcing. The method of support also affects the result. The somewhat square circle and the dumb-bell-shaped central nodal curve in some of Colwell's figures can be found also among the nodal figures yielded by Elsas's forced vibrations.

Vibrations of circular membranes. The principle of composition that has been developed in the present paper is evidently applicable to circular membranes, and assuming that the relative actual frequencies are the same as those given theoretically by a table of the roots of Bessel functions of the first kind, the following combinations among the lower partials appear probable: 0/2, 2/0; 0/5, 2/2; 3/2, 4/0. As in the case of plates it would seem that no two modes have exactly the same period, but since the overtones are very numerous (as may be seen from table 2, where the number of overtones in given intervals of several different vibrating systems have been compared) and the vibrations are relatively damped, compounded modes should occur fairly frequently. Any inequality of tension over the surface of the membrane will cause distortion, and the recent figures due to Schiller⁽⁷⁾ have the irregular features of figure 27 of the present paper, which was distorted by means of a clamp. The following compound modes can however possibly be recognized in his figures 4*a*, 4*b* and 4*c* respectively: 0/4, 1/2; 0/5, 2/2; 0/6, 2/2; and 0/3, 1/0 in his figure 5.

Table 2. Number of overtones in given intervals

Octaves	1	2	3	4	5	6	7	Source of information
Strings	2	4	8	16	32	64	128	
Free plates	1	4	8	14	27	51	84	Present observations.
Clamped plates	1	4	7	18				Tables and Franke.
Membranes	2	10	44	*c.* 157				From roots of Bessel Functions of first kind.

Comparison with circular plates clamped round the edge. Similarly it is possible to surmise which vibrating modes should combine in plates which are clamped round the edge, as is done in table 3, in which a few suggested combinations are placed by the side of the actual combinations that have been obtained with free circular plates. It may be noted, for example, that the 0/5 figure which we have seen compounded with a 1/2 mode in figures 4 to 6 above should, in the case of the clamped plate, combine with a 2/0 mode.

Table 3. Compounded normal vibrating modes

Free circular plate, experimental	Clamped circular plate, suggested
0/4 (4·10), 1/1 (3·99)	
0/5 (6·19), 1/2 (6·79)	0/5 (8·88), 2/0 (8·72)
	0/6 (11·27), 2/1 (11·8)
0/7 (11·7), 2/1 (11·74)	0/7 (13·8), 1/4 (13·7)

The frequencies of the free plate are given relatively to that of its gravest 0/2 mode, taken as 1, and those of the clamped plate are given relatively to that of its gravest 0/0 mode, taken as 1. It has been calculated⁽⁸⁾ that the frequency of the 0/0 mode of the clamped plate is approximately 1·92 times the frequency of the 0/2 mode of the free plate.

Cymbals. A few preliminary experiments with cymbals, kindly lent by Messrs Boosey and Hawkes, show that both the normal modes, in which the radii of the nodal circles and relative frequencies depend upon the type of cymbal, and also compounded modes can be produced. It will be interesting to continue these experiments, since the results could scarcely be obtained by analytical methods. The main difficulty is to obtain a powder which, though sufficiently mobile, will not slide off the plates.

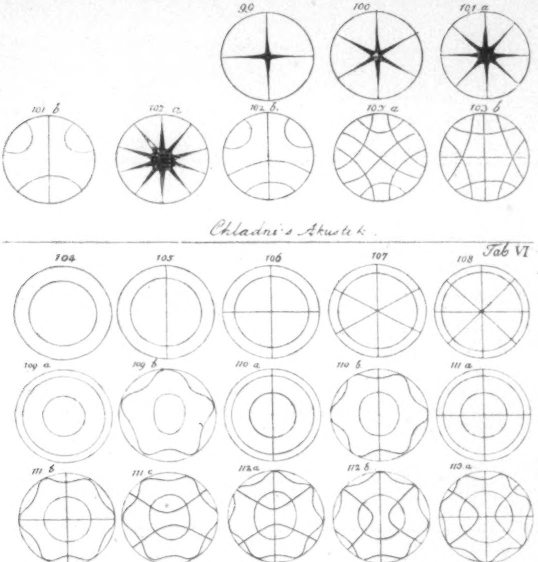
§ 5. CONCLUSIONS

All nodal designs, other than those corresponding to the normal modes of vibration, which can be produced on free circular plates or on other systems of revolution result from the combination of two or more normal modes of nearly equal period. This compounding of modes is made possible by the want of uniformity which generally exists in actual plates, and it is also made easier by an increase in the damping of the vibrations. The most usual cause of want of uniformity is a small variation in thickness. Another possible cause is variation of elasticity of the material in plates which have been rolled in one direction.

REFERENCES

(1) RAYLEIGH. *Theory of Sound*, **1**, 2nd ed. (*a*) p. 364; (*b*) p. 377.
(2) ELSAS, A. *Ann. Phys., Lpz.*, N.F. 19, 474 (1883).
(3) DEBYE, P. *Ann. Phys., Lpz.*, **25**, 819 (1908).
(4) FRANKE, G. *Ann. Phys., Lpz.*, **2**, 649 (1929).
(5) SHÜNEMANN, R. *Ann. Phys., Lpz.*, **24**, 507 (1935).
(6) COLWELL, R. C. *J. Franklin Inst.* **213**, 373 (1932).
(7) SCHILLER, P. E. *Z. Techn. Phys.* **15**, 294 (1934).
(8) See LAMB, H. *Dynamical Theory of Sound*, 2nd ed. p. 156 (1931).

PHYSICAL SOCIETY, VOL. 50, PT. 1 (M. D. WALLER, PT. 3, PLATE 1)


99
100
101 a
101 b
102 a
102 b
103 a
103 b
Chladni's Akustik
Tab VI
104
105
106
107
108
109 a
109 b
110 a
110 b
111 a
111 b
111 c
112 a
112 b
113 a
113 b
114
115
116 a
116 b
117 a
117 b
118 c
118 b
119 a
119 b
120
121 a
121 b
121 c
Tab VII
Fig 122
123
124
125
126
n
p

Figures 99–126 from Chladni, *Die Akustik.*

To face page 83

VIBRATIONS OF FREE CIRCULAR PLATES. PART 3: A STUDY OF CHLADNI'S ORIGINAL FIGURES

By MARY D. WALLER, B.Sc., F.Inst.P., Lecturer in Physics, London (Royal Free Hospital) School of Medicine for Women

Received 15 *October* 1937. *Read* 26 *November* 1937

ABSTRACT. The complete set of figures which Chladni produced on circular plates has been examined. It has been found that a second subsidiary normal vibrating mode, the nodal system of which consists of diameters, is in many of the figures compounded with a principal figure of nearly identical period. The manner of support and the manner of excitation make such combinations likely.

§ 1. CHLADNI'S ORIGINAL FIGURES ON CIRCULAR PLATES

THE *Entdeckungen über die Theorie des Klanges* which was published by Ernst Florens Friedrich Chladni in 1787 contains seventy-five copper-plate figures of his drawings of nodal lines produced on circular plates. Forty-three of these figures are reproduced in *Die Akustik* (1802, second edition 1830). They are shown in plates 1 and 2 of the present paper and were obtained at the Royal Institution through the kindness of Mr R. Cory the Librarian. The rest of the figures in the *Entdeckungen über die Theorie des Klanges* are, with but few exceptions to which reference will be made below, similar in character to those shown in plates 1 and 2. The study that has already been described in parts 1 and 2 of the present paper make it possible to see that most of the figures are a combination of two normal modes of vibration having nearly equal periods.

Of the single simple modes the highest number of diameters shown is five. Chladni, of course, produced a greater number of diameters than this, and his table of frequencies extends as far as eight diameters. He gives drawings for one and for two nodal circles; this is probably quite as much as could be managed by means of a bow applied at the edge of the plate. The highest single mode shown is that of figure 116*a*, which is of the 3/1 type. The relative frequency of this mode, according to table 1, of part 1, is 22·7.* There is considerable distortion in some of the earliest and latest figures, and this is no doubt due to a want of freedom in the manner in which the plate is supported.

The remaining figures all show a greater or smaller number of *Biegungen* or bendings in the nodal circles. Chladni paid special attention to these and gave a table⁽¹⁾ of the number generally associated with each figure, which number can also be counted directly on the figures reproduced in the present paper.

---

* It has been shown in part 1, § 4, that the relative frequencies are affected by the value of Poisson's ratio, so that the figures quoted here and below apply only approximately to glass plates.

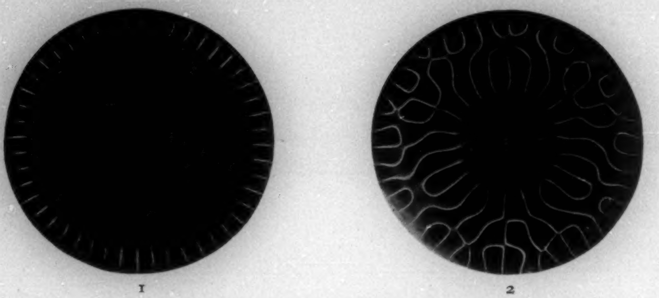
Figure 48 of part 2 of the present paper, which is a 0/13, 4/1 figure, was produced by bowing. It is of the same type as Chladni's, and each bend, or distance from crest to crest, in the wavy nodal circles evidently indicates the presence of two diameters of one of the combining modes, so that counting round the whole circle the number of bends in a figure such as 115 shows that an 8-diameter mode has combined with a 3-circle mode. In the case of figures which include obvious diameters, whether straight or curved, it has been found that the *Biegungen* diameters must be added to these in order to obtain the second vibrating mode.

Table 1 has been compiled according to this rule, the predominating mode being printed in black numerals while the frequency relative to that of the gravest mode, 0/2 (obtained from table 1 of part 1), is given in brackets. References to figures given in part 2 are followed by the letter *W*.

Table 1. Composition of Chladni's figures on circular plates

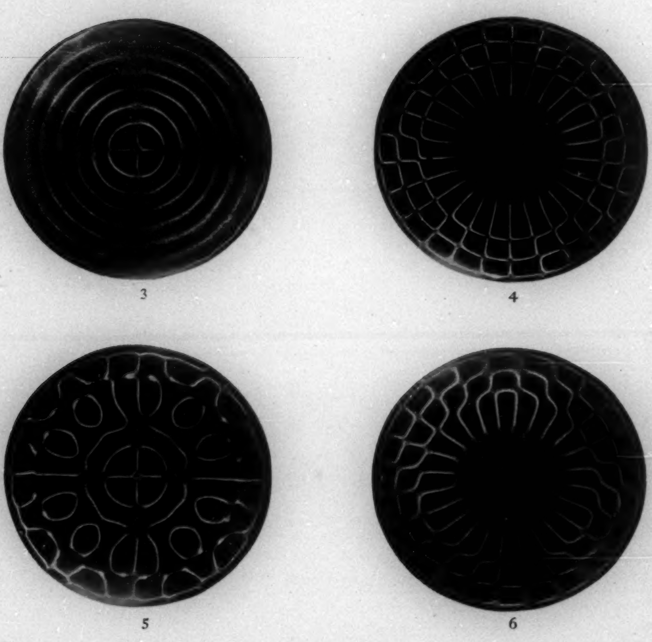
Figure	Modes and relative frequencies	Remarks
101*b*	0/4 (4·1), 1/1 (3·99)	Cf. figure 2, *W*, inverted, and also the less regular figures 125, 126 below
102*b*	0/5 (6·19), 1/2 (6·79)	Cf. figures 4–6, *W*, inverted
103*a*, *b*	0/8 (15·1), 2/2 (16·1)	Cf. 37, *W*
109*b*	**2/0** (7·50), 0/5 (6·19)	Chladni states that this was the only case in which he noted that the pitch was lower than that of the corresponding regular figure, here 109*a*. There are 6 instead of 5 *Biegungen* in the corresponding *Entdeckungen* figure, **2/0** (7·50), 0/6 (8·8)
110*b*	**2/1** (11·74), 0/6+1=0/7 (11·7)	Cf. 36, *W*
111*b*, *c*	**2/2** (16·1), 0/8 (15·1)	Cf. 103*a*, *b* and 37, *W*
112*a*, *b*	**2/3** (21·2), 0/7+3=0/10 (23)	
113*a*, *b*	**2/4** (27·1), 0/7+4=0/11 (27·6)	Cf. 38, 39, *W*
114	**2/5** (33·4), 0/7+5=0/12 (33)	Cf. 40, 41, *W*
115	**3/0** (16·4), 0/8 (15·1)	
116*b*	**3/1** (22·7), 0/9+1=0/10 (23)	
117*a*, *b*	**3/2** (29·4), 0/9+2=0/11 (27·6)	
118*a*, *b*	**3/3** (36·3), 0/10+3=0/13 (38)	
119*a*, *b*	**3/4** (43), 0/10+4=0/14 (44·5)	Cf. 42–47, *W*
120	4/0 (29·1), 0/12 (33)	In this and several neighbouring figures, and in those showing hyperbolic diameters, the imperfect freedom of the vibrations is specially manifest
121*a*, *b*, *c*	**4/1** (37), 0/13 (38)	Cf. 48, *W*
122	Less free, distorted 0/2	
123, 124	Distorted 0/3 (2·29)	
125, 126	Distorted 0/4 (4·10) and 1/1 (3·99)	

Additional figures in the Entdeckungen über die Theorie des Klanges. There are several more variants of the 0/5 (6·9), 1/2 (6·79) nodal figure to be seen in Chladni's earlier publication. The remaining figures are similar to those already considered but are compounded of higher partials, the last of which is a 7/0, 0/22 (110) combination evidently made on a plate which was not quite free.



1 2

Figures 1, 2. Plate excited at the edge with a bow.



3 4 5 6

Figures 3 to 6. Plate excited between the centre and the edge with solid carbon dioxide; see table 2.

To face page 85

§2. NOTE ON METHODS OF PRODUCING VIBRATION IN PLATES

The six figures of plate 2 which were produced on a centrally supported plate of diameter 46·2 cm. and thickness 2 mm. illustrate the possibilities of producing higher partials by means of a bow or of solid carbon dioxide. The first two figures were made with a small violin bow plentifully supplied with powdered resin, and the last four with solid carbon dioxide which was applied between the centre and circumference of the plate. Data regarding these figures are given in table 2. The essential freedom of these two methods of excitation is shown by the single-mode nodal designs of figures 1, 3 and 4.

Table 2

Figure	Nodal design	Approximate frequency (c./sec.)	Approximate frequency relative to that of 0/2 mode
	Single mode		
1	0/24	4200	127
3	7/2	5300	160
4	3/13	5100	154
	Compounded modes		
2	0/23, 3/11	3900	118
5	5/2, 1/12, etc.	2080	65
6	3/12 (0/25)	4360	130

The difference in character between the decorative designs produced by excitation at the edge and near the centre respectively, is specially noticeable in figures 2 and 6. In figure 2 the 0/23 mode is combined with a 3/11 mode of smaller amplitude, while in figure 6 a 3/12 mode is combined with a 0/25 mode of very much smaller amplitude. There is a threefold motif in both figures which are very interesting to compare.

It is evident that by varying the point of application of the solid carbon dioxide, and by the appropriate use of a divider to introduce constraints and damping, it should be possible to obtain a large number of very beautiful designs.

The figures may be compared with one of Colwell's high-frequency figures(2) produced with a magnetostriction oscillator, in which an 8/1 or 9/1 component is, I think, present. The frequency of this figure is stated to be some submultiple of 15,000 c./sec.; the size of the circular plate used is not specified.

An exhaustive reference to electrical methods of producing Chladni figures cannot be made here, but a brief mention of some purposes for which they have been employed when the two simpler methods could not be used may not be out of place. Thus Wood and Smith(3) and Colwell and Hall(4) have employed a magnetostriction oscillator to produce large numbers of nodal circles, the former for the purpose of determining the velocity of sound in non-metallic as well as in metallic circular sheets. Wood(5) has also used the same method to excite small circular discs. Franke(6) has produced forced oscillations in clamped circular plates. Andrade and Smith(7) have used an electromagnet in order to control the amplitude of vibration of steel plates in their study of the manner of formation of sand figures. In this last connection it is interesting to compare such figures as 1 and 3 of plate 2, where in the first figure the amplitude of vibration is small except round the edge, while in figure 3, the plate is vibrating vigorously over its entire surface.

The main purpose of this concluding section, however, is to draw attention to the very simple and effective methods of excitation which continue to be available for most general purposes—the bowing method for producing diameter figures and decorative figures of a specified type, and the solid-carbon-dioxide method for producing not only these but also the circle and circle-diameter figures and the large variety of designs which can be obtained by altering the position of excitation over the surface of the plate.

REFERENCES

(1) CHLADNI. *Die Akustik*, 2nd ed. p. 128 (1830).
(2) COLWELL, R. C. *Nature, Lond.*, **133**, 258 (1934).
(3) WOOD, A. B. and SMITH, F. D. *Proc. Phys. Soc.* **47**, 149 (1935).
(4) COLWELL, R. C. and HALL, L. R. *J. Acoust. Soc. Amer.* **8**, 60 (1936).
(5) WOOD, A. B. *Proc. Phys. Soc.* **47**, 794 (1935).
(6) FRANKE, G. *Ann. Phys., Lpz.*, **2**, 649 (1929).
(7) ANDRADE, E. N. DA C. and SMITH, D. H. *Proc. Phys. Soc.* **43**, 405 (1931).

A NOTE ON THE OPTIMUM COUNTING-TIME FOR MEASURING THE INTENSITY OF A RADIOACTIVE SOURCE

BY J. TANDBERG

Received 17 *September* 1937. *Read in title* 12 *November* 1937

ABSTRACT. When the intensity of a radioactive source is measured by means of a Geiger-Müller counter, maximum accuracy is obtained by continuing the counting for a finite time which depends on the average life of the radioactive source and on the intensity of the background interference.

WHEN particles from a radioactive source are counted by means of a Geiger-Müller tube a certain background of adventitious impulses will always be present. If the period of the source is a short one it is of no use to extend the counting for a long time, since the natural fluctuations of the background will have a detrimental influence on the accuracy of the result. In figure 1 the straight line *A* represents the mean progression of the number of impulses counted, as a result of the background alone. Curve *B* may represent an actual count, involving the fluctuations of the background.

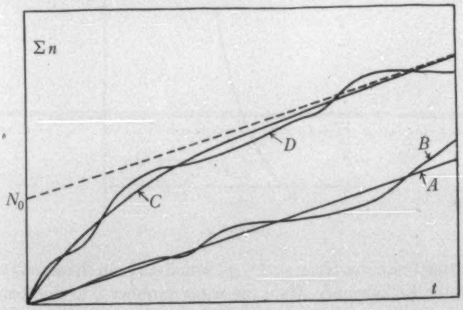


Figure 1.

The smooth line *C* represents the ideal counting of particles from a weak radioactive source, including the background, such as would occur if the fluctuations were negligible. The irregular curve *D* around *C* represents an actual counting series, inclusive of the fluctuations. It is obvious that if we wish to count the total quantity of particles emitted from the radioactive source during a very long time, we shall not be helped by means of an extended counting series, because the fluctuations will soon cause the curves D and B to be confused. For a very short series, on the other hand, the fluctuations of the source itself may easily predominate and the result will accordingly be uncertain. An optimum counting-time is therefore to be expected.

Supposing we have an unknown number N_0 of impulses, latent at the beginning, the decay constant λ and the background of b impulses per minute being known,

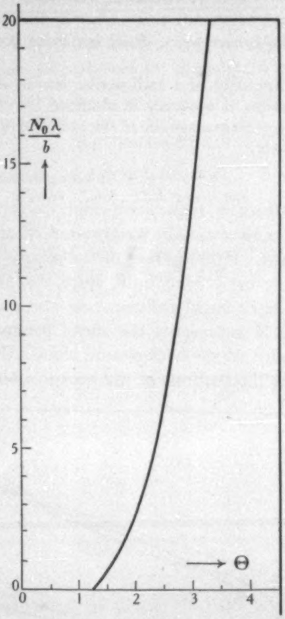


Figure 2.

we shall get during t minutes $N_0(1-e^{-\lambda t}) \pm \zeta$ impulses from the source and $bt \pm \sqrt{(bt)}$ impulses from the background. Here the mean number ζ of fluctuations is determined by the expression:

$$\zeta^2 = Z\,(1 - Z/N_0) = N_0\,(e^{-\lambda t} - e^{-2\lambda t}),$$

where Z stands for the first of the above expressions.

Thus we have during t minutes a total number of impulses:

$$\Sigma n = Z + bt \pm \sqrt{(\zeta^2 + bt)}.$$

In order to obtain the least erroneous value of N_0 we will set out to find the time t^* for which the mean relative fluctuations $1/Z\sqrt{(\zeta^2+bt)}$ shows a minimum. We proceed to investigate the square of the expression and thus obtain the function

$$f(t)=\frac{1}{Z^2}\left\{Z\left(1-\frac{Z}{N_0}\right)+bt\right\}=\frac{1}{N_0}\left\{\frac{e^{-\lambda t}}{1-e^{-\lambda t}}+\frac{bt}{N_0(1-e^{-\lambda t})^2}\right\}.$$

Making the first derivative $f'(t)$ equal to 0 and transforming the expression we get

$$\frac{N_0\lambda}{b}=e^{\lambda t^*}-\frac{2\lambda t^*}{1-e^{-\lambda t^*}}.$$

An investigation of the second derivative will confirm that t^* corresponds to a minimum of $f(t)$.

Denoting $\lambda t^*=\Theta$ we may regard Θ as the optimum time of counting, expressed in terms of the average life $(1/\lambda)$ of the radioactive substance.

Now $N_0\lambda$ represents the initial intensity of the source, corrected for the effect of the background. Thus the quotient $N_0\lambda/b$ may be considered as the relative initial intensity of the radioactive source in terms of that of the background. The graph in figure 2 gives the relation between $N_0\lambda/b$ and Θ for small values of Θ. If we consider a numerical example with radioactive indium, for which $\lambda=0{\cdot}01274$ min.$^{-1}$, having an initial activity equal to the background, it will be seen that it is of no use to continue the measurement longer than $\Theta=1{\cdot}6$ or about 2 hours. An extended counting of impulses would give results of decreasing accuracy.

THE RATIO OF THE MASSES OF THE FUNDAMENTAL PARTICLES

By H. T. FLINT, Reader in Physics, University of London,
King's College

Received 22 *October*, 1937. *Read* 12 *November* 1937

ABSTRACT. A discussion of the nature of the equations of the quantum theory, based upon the theory of relativity, having indicated that difficulties of a fundamental character will arise when dimensions less than the electron-radius are concerned, it is pointed out that the idea that such dimensions are not observable must be included in a geometrical description in physics. The electron-radius is thus the minimum length we discover in our measurements relating to the interaction of particles. But the principle of minimum proper time applied to the track of a heavy particle M_0 shows that the particle is in effect a time scale whose finest division is h/M_0c^2. In the theory of relativity the conception of a minimum length e^2/m_0c^2 becomes equivalent to the conception of a minimum interval of proper time e^2/m_0c^3. The argument shows that these two intervals are of the same order of magnitude and leads to a simple relation between the mass ratio of the proton and electron and the fine-structure constant.

In a communication published in these *Proceedings*[(1)] a short time ago, Dirac's quantum equation was developed from a new point of view. The details of the development are set forth in that communication, but the basis of the procedure may be briefly stated here. The underlying idea is that the quantum equation, written down for the case of a single charged particle in an electromagnetic field in the form required by the theory of relativity, is the representation of a law of natural gauging. The procedure is nothing more than an appeal to mathematical form based on Weyl's metrical theory and upon Eddington's generalization of it. From the physical point of view it is preferable to Weyl's system of gauging in that the idea of parallel displacement which has to be included in the geometrical and metrical description of the physical world can be correlated with actual displacements taking place in that world. The natural law of gauging deduced from the equation gives to the conception of parallel displacement the physical content lacking in the theory of Weyl.

The change of length which a vector undergoes in such a displacement was shown to be

$$\frac{\delta l}{l}=\frac{2\pi i}{h}\left(m_0c^2\,\delta\tau-\frac{e}{c}\phi_m\,\delta x^m\right) \qquad \text{......(1).}$$

We are here thinking of a track along which a charge e associated with a rest mass m_0 is travelling. A vector of length l with one end on the track is displaced parallel to itself so that the co-ordinates of the end change by $(\delta x^1\ \delta x^2\ \delta x^3\ \delta x^4)$. $\delta\tau$ is the element of proper time corresponding to the displacement. ϕ_m is a typical component of electromagnetic potential.

Some conclusions with regard to the limit of application of the theory were given at the end of the previous communication. The question has been further discussed(2) and it has been shown that difficulties of a fundamental character are encountered when we attempt to solve any problem in which ultimate units e of electric charge lie closer together than a distance of the order e^2/m_0c^2, m_0 denoting the rest mass of the electron. The discussion suggests that within a domain of such linear dimensions our customary conception of space and time breaks down, and that it would be surprising if, with this conception, smaller distances made their appearance in the physical world. Thus if we adopt a geometrical description of the physical world and if we take this point into consideration, the postulate must be included that points within such small domains are indistinguishable from one another. There appears in this way a smallest dimension l_0 which we describe as e^2/m_0c^2, where m_0 is a constant having the dimensions of mass. Introduced in this way m_0 is no longer subject to the limitations which characterize it when we recognize it as the mass of a particle to which we give a definite structure. But if we can imagine ourselves starting out with a constant having the dimensions of mass and introduced in this way, its appearance in any equation would naturally suggest to the mind of a physicist trained in the laws of mechanics the existence of a particle of mass m_0. If the length, l_0, has the fundamental significance which we now suggest, it will be certain to be discovered in our investigations in physics and it may appear in a connexion not necessarily associated with the electron. Prof. A. March(3), quite independently of these discussions, has made the assumption that in a four-dimensional world there is no means of distinguishing between points separated in space-time by a distance less than e^2/m_0c^2. This view he developed in two papers on "The geometry of smallest spaces", but later he modified his views somewhat in the foundation of a statistical metric in which the idea that an electron is not to be defined within a sphere of the above radius l_0 is an essential feature. He shows that the difficulties associated with the self-energy of the electron can in this way be avoided, and in a paper on the gravitational energy of the photon(4) he points out the occurrence of the length l_0 in a phenomenon which has nothing to do with the electron.

In the author's earlier communication already referred to(1) the principle of minimum proper time was deduced from equation (1). This principle, originally developed from the old quantum conditions relating to action and momentum(5), has been established in a variety of ways(6). It states that when a neutral particle of rest mass M_0 is considered, it is impossible to associate with its motion any interval of proper time less than h/M_0c^2; and the same is true of a charged particle in a weak field. Both this principle and the idea that l_0 is the smallest length occurring in the physical world are contained in the gauging law (1), for as we have shown before(1, 2) the quantum conditions are replaced by the rule that in any parallel displacement which has a physical counterpart the change δl is always zero; or in other words, the quantity in the brackets on the right-hand side of (1) is always an integral multiple of h.

We thus include in one quantum law two fundamental lengths h/m_0c and e^2/m_0c^2.

This view of the nature of the length which we usually describe as the radius of the electron gives a new approach to problems which have been explained by assuming the existence of an elementary particle carrying a charge e, possessing mass m_0, and of the form of a sphere of radius $k\,(e^2/m_0c^2)$, where k is of the order unity.

The alternative to the introduction of the electron as a particle is the idea that the smallest interval of proper time observable in the physical world is of the order e^2/m_0c^3, where m_0 simply occurs as a constant of the dimensions of mass.

This particular magnitude arises, according to the usual conception, in a consideration of the interaction of fundamental particles with one another. To these fundamental particles we assign masses M_0 and m_0, described as the masses of a proton or neutron and of an electron. For the present purpose it is not necessary to distinguish between the masses of the two heavy particles.

The principle of minimum proper time allows us to regard the particle of mass M_0 as a scale of time of which the smallest division is h/M_0c^2.

This scale of time is sufficiently finely divided to enable us to measure l_0/c, so that the two intervals are of the same order of magnitude. This view may be expressed as an equation thus

$$\frac{h}{M_0c^2}=k\,\frac{e^2}{m_0c^3} \qquad \ldots\ldots(2),$$

where k is of the order unity.

Thus in our calculations we shall be concerned with the mass ratio M_0/m_0, where

$$\frac{M_0}{m_0}=\frac{2\pi}{k}\left(\frac{hc}{2\pi e^2}\right) \qquad \ldots\ldots(3).$$

Experiments which measure M_0/m_0, e, c and h, or the fine-structure constant $2\pi e^2/hc$ directly, will give the value of k.

If we use a particle description of the phenomena instead of the geometrical one, we shall describe the ratio as the ratio of their masses.

The relation (3) is satisfactory from the point of view of order of magnitude, if M_0/m_0 is the ratio of the mass of the proton to that of the electron.

One hesitates to go farther with this equation in order to deduce from it more than an equality of magnitudes, especially as the determination of k is not altogether satisfactory. But it is interesting to examine the agreement afforded by making use of a value of k which has been suggested by the view that we are dealing with an electron with a definite structure and satisfying certain energy relations. Values of k suggested by the classical theory are $\frac{2}{3}$ and $\frac{4}{5}$, according to the nature of the distribution of the charge. Fürth has attempted a calculation(7) more in accordance with new quantum considerations. He has pointed out that it becomes difficult to consider an electron as a sharply defined structure and considers a length which he describes as an equivalent radius, the value of k according to him being $\frac{15}{32}$.

We shall take this value since Fürth's calculation rests upon modern ideas, though according to our view the constant k must be independent of any theory about the structure of a particle.

With this value we obtain the agreement described below. But from a study of the literature on the values of the mass ratio and of the fine-structure constant it would appear that the last word has not been said upon this subject.

On one hand we have Eddington's suggestion that $hc/2\pi e^2$ is integral and equal to 137, and on the other the value 137·2 was suggested a few years ago. Recent contributions to the discussion suggest a value closer to 137, but in the opinion of some spectroscopists it is not yet possible to be certain of this value within a margin equal to 0·1.

A similar difficulty occurs with regard to the mass ratio. Recent contributions to the discussion appear to point to a value close to 1839, although there is one suggestion that the value is 1837.

These numbers serve to illustrate the agreement of the formula when Fürth's value is taken for k. For the lower number 137 the ratio is 1836·4 and for the higher value 137·2 the ratio is 1839·0.

Our object here is not to lay stress on the actual values obtained but to point out the simple relation between the mass ratio and the fine-structure constant, and the new character which the ratio acquires from the assumption of the existence of an indivisible scale of time.

REFERENCES

(1) FLINT. *Proc. Phys. Soc.* **48**, 433 (1936).
(2) FLINT. *Proc. Roy. Soc.* A, **159**, 45 (1937).
(3) MARCH. *Z. Phys.* **104**, 93, 161; **105**, 620; **106**, 49 (1936), (1937).
(4) MARCH. *Z. Phys.* **106**, 291 (1937).
(5) FLINT. *Proc. Roy. Soc.* A, **117**, 630 (1927).
FLINT and RICHARDSON. *Proc. Roy. Soc.* A, **117**, 637 (1927).
(6) RUARK. *Proc. Nat. Acad. Sci., Wash.*, **14**, 322 (1927).
LANDAU and PEIERLS. *Z. Phys.* **69**, 56 (1931).
SCHROEDINGER. *S.B. Preuss. Akad. Wiss.* **12**, 238 (1932).
(7) FÜRTH. *Z. Phys.* **57**, 429 (1929).

DISCUSSION

Mr J. GUILD. When surprisingly accurate numerical agreements, such as that given in the present paper, drop out of theoretical equations, it is wise nowadays to look carefully for the possibility of circular reasoning before accepting them as confirmation of the theory. The danger of this is now very great, owing to the impossibility of anyone carrying in mind more than a fragmentary précis of the large volume of literature that has been written round the few constants h, c, e, M_0 and m_0. I think we can find an example of this danger in the present case. Flint's value of M_0/m_0 depends on Fürth's value of k. There are numerous assumptions in Fürth's paper which one might question if that paper were the subject of discussion, but as it is not we may take it at its face value in considering its bearing on the result of the present paper. On Fürth's theory, the quantity k must obey the relation

$$M_0/m_0 + m_0/M_0 + 2 = hc/ke^2 \qquad \text{......(A),}$$

which is Fürth's equation (18) translated into the symbols of the present paper. All the quantities except *k* are known, so *k* can be obtained directly from this relation.

Fürth, it is true, then proposes a charge-distribution for the electron, and a definition of the electron radius, which gives the correct value of *k* very closely. This must not, however, be regarded as an independent estimate of *k* confirming the relation (A). This relation requires no confirmation on Fürth's theory. It is necessarily true in virtue of his previous treatment, whatever the structure of the electron may be. Had his proposed theory of electron structure not led to this value, that theory would have been at fault, and not relation (A), which is an integral part of his main theory and in fact implies the definition of the constant *k* as used by him.

As M_0/m_0 is nearly 2000, relation (A) implies that to within about 1 part in 1000

$$M_0/m_0 = hc/ke^2, \quad \text{or} \quad k = \frac{m_0}{M_0}\frac{hc}{e^2}.$$

If we insert this value of *k* in Flint's equation (2) we find that it reduces to an identity and will necessarily give back the same value of the proton-electron mass ratio that was put into it via Fürth's *k*.

Even were this not so, no value given by Fürth's theory can legitimately be quoted as confirming the hypothesis of the present paper, which is that distances less than e^2/m_0c^2—about the diameter of the electron—are without physical significance. Fürth's structure of the electron, necessary to give a value of *k* consistent with relation (A), supposes a spacial distribution of charge both inside and outside the radial distance, and implies the applicability of ordinary integration with respect to distance right into the centre. Further, Fürth's theory, in common with many others, leads to a value of the radius of the proton which is to that of the electron in the inverse ratio of the masses; see his equations (4), (13) and (17), and his final numerical values. On the author's theory the world cannot accommodate anything smaller than an electron, certainly not an object only about a two-thousandth of its size, nor can distance possess integrability within the electron radius. He must reject these corner stones of Fürth's investigation, and with them of course Fürth's value of *k*, as incompatible with the theory he is seeking to establish.

The view that space and time lose their significance below certain limiting values is a purely metaphysical escape from the difficulties which confront mathematical analyses, of the types so far developed, when carried beyond these limits. Unless there is some conceivable experiment which would distinguish discontinuities in space or time, such discontinuities cannot exist even as a pragmatic hypothesis. No such experiment can be formulated. A conceivable experimental significance is the scientific criterion of actual or possible existence, and this really provides the answer to those who claim that the contemplation of mathematical form is a substitute for the contemptuously dismissed model. We cannot, even in imagination, construct an experiment from symbols. We have to conceive any experiment in terms of bits of reality, actual or hypothetical; not symbols but the things to which the symbols refer; in other words, the constituents of a model. Any attempt to do this in the present case leads at once to logical contradictions. The author relates his minimum length and time by the relativistic formula in which space and time intervals are related by the boundary velocity c. What is the significance of velocity in a region of non-existent space and time? Further, how can we assess magnitudes in the ordinary space and time measures to such regions? The quantity l_0 is a length and yet is supposed to give a measure of the extent of some kind of region in which length is physically meaningless—some kind of gap in the structure of length. Similarly, we are given a time measure of the *duration* of gaps in the structure of time. Obviously if it were possible to conceive of discontinuities in space and time their extent would have to be measured in some other kind of dimensions altogether. We should have to conceive of space and time as having phenomenal existence *in* a continuum of some other kind. Discontinuity of space or time would then be conceivable and describable in terms of a metric appropriate to this non-temporal, non-spatial continuum. But the introduction of ideas of this kind with no empirical basis whatever has no justification. Space and time form the ultimate background of phenomena in all the equations of physics, which, therefore, cannot logically lead to the conception of discontinuity in that ultimate background itself.

We must avoid the tendency, when confronted with analytical difficulties, to invest nature with properties whose only function is to conceal our troubles. Eddington has warned us, in connexion with cosmic problems, of the danger of constructing a wall at the edge of the universe over which we can throw our unsolved problems. The quantum physicist does not carry his difficulties to the edge of the universe to dump them over the wall, but wants apparently to stuff them into holes in time and space. It is better to leave them lying about as a reminder that there is still work to be done in tidying up the unsolved problems of analysis.

AUTHOR's reply. Mr Guild's criticism falls into two distinct parts, the first of which is concerned with arithmetical agreement and the second with considerations of a general character. I am not altogether out of sympathy with the opinions he expresses in the latter part, but he makes no statement which invalidates the basis on which the communication rests. This is that the description in terms of space and time is subject to conditions laid down by the quantum theory.

The first part of his criticism is more specific but the communication is concerned only with the equality of the orders of two magnitudes, not with arithmetical agreement. The value of k to which he refers is introduced merely to illustrate the agreement obtained, and it is expressly stated to be no part of the theory under discussion, which has so far not succeeded in deducing its value.

Mr Guild's remarks upon Fürth's paper, and in particular his reference to equation (A), show that he has misinterpreted its object. The constant k is calculated by Fürth independently of the ratio M_0/m_0, just as it was calculated long ago in the classical theory without any reference to this ratio. Fürth's remark on equation (A) makes the point clear. "In order to obtain M_0/m_0 we need the value of k."

ATOMIC SCATTERING FACTORS OF ALUMINIUM, POTASSIUM CHLORIDE AND COPPER FOR X RAYS

By G. W. BRINDLEY, M.Sc., Ph.D., Mackinnon Student of the Royal Society

AND

P. RIDLEY, B.Sc., Physics Laboratories, University of Leeds

Received 27 *September* 1937. *Read in title* 12 *November* 1937

ABSTRACT. The intensities of X-ray reflections from powders are placed on an absolute scale by comparison with reflections either from potassium chloride or from aluminium, the absolute values obtained by James and Brindley for these substances being taken as standard values. It is pointed out that the results obtained by standardizing with respect to aluminium are consistently about 10 per cent higher than those obtained when potassium chloride is used as the standard. New determinations of the scattering factors of potassium chloride and aluminium are made by the powder method, and it is shown that whereas the aluminium values agree well with the previous measurements made by James and Brindley, the new values for potassium chloride differ by an amount which explains the discrepancy mentioned above. The theoretical scattering factors of K^+ and Cl^- are recalculated on the basis of Hartree's latest wave functions, in which allowance for electron-exchange is made. Good agreement is found between the present measurements for potassium chloride and the theoretical results. The scattering factor of Cu^+ also is calculated with and without allowance for electron-exchange, and the results are compared with experimental data for metallic copper.

§ 1. INTRODUCTION

In connexion with the absolute measurement of the intensities of X-ray reflections from powders by the methods described in the preceding paper, it was found necessary to re-examine the intensities reflected by potassium chloride and aluminium powders, since it is by comparison with reflections from these substances that reflected intensities from powders are placed on an absolute scale. For this purpose it is usual to take as standard values the absolute measurements of James and Brindley(13) for potassium chloride and of James, Brindley and Wood(14) for aluminium; these were obtained by the ionization method with large single crystals. Reflections from sodium chloride also are used as standards by some workers, and the measurements of James and Firth(12) are then used. It has been found(1), however, that the results obtained by standardizing with respect to aluminium are consistently higher than those obtained when potassium chloride is used as the standard, the difference amounting to about 10 per cent in measurements of atomic scattering factors. These results suggested that incorrect values were being assumed for either the potassium chloride or the aluminium reflections, or both, and it was considered essential, therefore, to discover the source of these discrepancies before either substance could be regarded as a satisfactory standard.

In the present paper, experimental values, obtained by the powder method, are given for the scattering factors of potassium chloride and aluminium for copper K_α radiation. The relative values for aluminium are shown to be in close agreement with the measurements made by James, Brindley and Wood for single crystals of aluminium and also with theoretical values based on the wave functions calculated by Hartree's method(4). The absolute scattering factor of potassium chloride is then obtained from a comparison of the reflections from powdered potassium chloride with suitable reflections from powdered aluminium. The theoretical scattering factors of K^+ and Cl^- have been recalculated on the basis of the recent results of D. R. and W. Hartree(9) for the electron-distributions of these ions, in which allowance for electron-exchange is made. The change in the scattering factors due to allowance for electron exchange is shown to be small but in such a direction as to increase the discrepancy with the previous measurements of James and Brindley. The new experimental values for potassium chloride, however, are in good agreement with the theoretical values.

The origin of the previous discrepancy is difficult to trace. It was clearly not due to anything of a fundamental nature, and the only explanation appears to be that it arose from some peculiarity or characteristic of the large crystals which were used in the experiments. This is also the opinion of Prof. James, who discusses the matter briefly in a note accompanying this paper.

Results are also given for the scattering factor of Cu^+ calculated with and without allowance for electron-exchange, and a brief comparison is made with experimental results for metallic copper.

§ 2. EXPERIMENTAL

The experiments were carried out with the X-ray camera and by the methods described in the preceding paper. The intensities were measured with a microphotometer by a null method of measurement. The films were developed and fixed under standard conditions, and the exposure times were so chosen that the maximum blackness of the lines came well within the range for which photographic blackness and X-ray intensity are proportional. Copper K_α radiation was used throughout the investigation. The relative intensity of reflection, I_r, is given by the relation

$$I_r/A \propto pF^2\phi(\theta) \qquad \ldots\ldots(1),$$

where

$$\phi(\theta) = (1+\cos^2 2\theta)/\sin\theta \sin 2\theta$$

and

$$A = \sin(2\theta-\alpha)/[\sin(2\theta-\alpha)+\sin\alpha].$$

Also p is the multiplicity factor for the reflection, F is the reflected amplitude per unit cell, θ is the Bragg angle of reflection and α the angle between the incident beam and the powder plate. For potassium chloride, $F=4\,[f_T(K^+)+f_T(Cl^-)]$, where f_T denotes the effective atomic scattering factor at temperature T; for aluminium, $F=4f_T(Al)$. From relative measurements of I_r/A we obtain by means of relation (1) relative values of $f_T(K^+ + Cl^-)$, or $f_T(Al)$.

§ 3. RESULTS FOR ALUMINIUM

Since aluminium cannot be produced in a finely divided state by chemical means, a fine powder was prepared by filing and the finest particles were separated by means of a sieve having 350 meshes to the inch. The clear resolution of the $K\alpha_1\alpha_2$ doublet for high-order reflections indicates that there is little or no distortion in the filed powder. Any small distortion could be removed by suitable annealing, but this would be of doubtful value in the present investigation since removal of strain by annealing would probably be accompanied by crystal-growth and even if this is only small it may produce appreciable extinction effects. We have therefore preferred to use the powder in the unannealed condition; the results obtained suggest that any distortion produced by the filing has a negligible effect on the X-ray intensities.

Table 1. A comparison of the scattering factors of aluminium obtained from powder measurements, single-crystal measurements, and theoretical calculations

1	2	3	4	5	6	7	8	9	10
Spectra	Powder measurements			Single-crystal measurements (J., B. and W.)					Theoretica values of f_T for copper K radiation
	Copper K_α radiation			Molybdenum K_α radiation			Dispersion correction	Copper K_α radiation f_T	
	I_r/A relative	f_T relative	f_T absolute	f_T observed	Extinct. correction	f_T corrected			
111	362·0	2·40	8·62	7·08	1·38	8·46	0·11	8·57	8·63
200	166·0	2·22	7·98	6·63	1·33	7·96	0·11	8·07	8·13
220	*100·0*	1·86	*6·68*	—	—	6·58*	0·10	6·68	6·74
311	107·4	1·63	5·85	—	—	5·75*	0·10	5·85	5·91
222	31·2	1·58	5·67	5·25	0·27	5·52	0·10	5·62	5·69
400	—	—	—	4·46	0·19	4·65	0·09	4·74	4·80
331	48·4	1·16	4·16	—	—	4·06*	0·09	4·15	4·20
420	47·8	1·12	4·02	—	—	3·90*	0·09	3·99	4·04
422	53·7	0·95	3·41	—	—	3·32*	0·09	3·41	3·46
333	—	—	—	2·96	0·03	2·99	0·08	3·07	—
600	Unobtainable			2·24	0·00	2·24	—	—	—
444				1·57	0·00	1·57	—	—	—
800				1·08	0·00	1·08	—	—	—
555				0·87	0·00	0·87	—	—	—

* Values obtained by graphical interpolation.

The results are set out in table 1 and are compared with the absolute measurements made by James, Brindley and Wood for single crystals of aluminium, and also with the theoretical values calculated by the Hartree method. Column 1 gives the indices of the reflections, column 2 the observed values of I_r/A obtained from the powder photographs for copper K_α radiation relative to 100·0 for the 220 reflection, and column 3 the relative f_T values calculated by means of relation (1). The single-crystal measurements of James, Brindley and Wood are summarized in columns 5, 6 and 7; column 5 gives the observed f_T values, column 6 an extinction correction, and column 7 the f_T values corrected for extinction. The extinction correction was obtained by assuming the theoretical f values derived by Hartree's method for the 111 and 200 reflections and was then calculated for the higher-order reflections by means of a formula due to Darwin. The f_T values for the 111 and 200 reflections are therefore the theoretical values modified by the appropriate temperature factor calculated from the experimental results given in the paper. The extinction correction falls off rapidly with increasing order of the reflections, and the higher-order f_T values are practically independent of the precise values assumed for the 111 and 200 reflections. In these experiments molybdenum K_α radiation was used and reflections were measured of higher order than can be obtained with copper K_α radiation. Before the powder measurements can be compared with the single-crystal measurements a small dispersion correction is necessary, and this has been calculated from the data given by Hönl(11). If $f_{\lambda\to 0}$, f_{Mo} and f_{Cu} are the scattering factors respectively for short waves, molybdenum K_α and copper K_α radiations, then in the usual notation,

$$f_{\mathrm{Cu}} = f_{\lambda\to 0} - \Delta f_{\mathrm{Cu}}$$

and

$$f_{\mathrm{Mo}} = f_{\lambda\to 0} - \Delta f_{\mathrm{Mo}},$$

so that

$$f_{\mathrm{Cu}} = f_{\mathrm{Mo}} - \Delta f_{\mathrm{Cu}} + \Delta f_{\mathrm{Mo}}.$$

For atoms vibrating at temperature T, we have

$$f_{T,\,\mathrm{Cu}} = f_{T,\,\mathrm{Mo}} + (\Delta f_{\mathrm{Mo}} - \Delta f_{\mathrm{Cu}})\, e^{-M},$$

where $M = 0{\cdot}01182\,(h^2+k^2+l^2)$ according to the measurements made by James, Brindley and Wood. From Hönl's data, we have $\Delta f_{\mathrm{Cu}} = -0{\cdot}18_1$ and $\Delta f_{\mathrm{Mo}} = -0{\cdot}06_5$. The dispersion correction $(\Delta f_{\mathrm{Mo}} - \Delta f_{\mathrm{Cu}})\, e^{-M}$, is tabulated in column 8 and the resulting f_T values for copper K_α radiation in column 9.

The relative f_T values from the powder measurements have been placed on an absolute scale by assuming f_T for the 220 reflection to be 6·68 as given by the single-crystal measurements; the results are given in column 4. The powder values in column 4 can now be compared with the single-crystal values in column 9; the agreement between the two sets of values is everywhere within the limits of experimental error and appears to justify the use of powdered aluminium as a satisfactory substance for standardizing the intensities of X-ray reflections from powders.

In column 10 are given the theoretical f_T values calculated by the Hartree method with the appropriate corrections for temperature and dispersion for copper K_α radiation. These values are based on the wave functions calculated by the self-consistent-field method, but without allowance for the effects of electron-exchange. In the case of K^+, Cl^- and Cu^+, allowance for electron-exchange has the effect of raising the scattering factors by a small amount, and presumably the effect will be in the same direction for aluminium. It is not possible to make any reliable estimate of the magnitude of the effect from the results for the other ions, but it will probably be small and will not affect very largely the good agreement between the calculated scattering factor and the observed values.

§4. RESULTS FOR POTASSIUM CHLORIDE

Finely divided potassium chloride powder was produced by dissolving metallic potassium in alcohol and passing hydrochloric acid gas or chlorine through the solution. Relative values of I_r/A were obtained in the manner already described and hence the relative values of f_T ($K^+ + Cl^-$); these are given in columns 3 and 4 of table 2. The absolute values of f_T were obtained by comparing the 420 and 422 reflections of potassium chloride with the 220 and 311 reflections of aluminium by the method of substituted powder layers described in the preceding paper; the results of the comparison are set out in the lower part of the table. The linear absorption coefficients of potassium chloride and aluminium for copper K_α radiation were taken as 243·5 and 131·8 respectively; the uncertainty in these values is probably less than 1 per cent, so that if both errors act in the same direction the final error in f_T for potassium chloride will not be greater than 1 per cent, since f_T depends on $\sqrt{\mu}$.

The scattering factor f for the atoms at rest, calculated by means of the usual equation

$$f_T = fe^{-M},$$

is tabulated in column 7. The temperature factor e^M in column 6 of the table is calculated from the expression

$$M = 1{\cdot}689\,(\sin^2\theta)/\lambda^2,$$

where λ is in angstrom units. This expression is obtained from equation (10) of the paper by James, Brindley and Wood$^{(14)}$ and is derived from experimental data.

To facilitate comparison with the theoretical scattering factors which are valid for sufficiently small waves such that $\lambda \ll \lambda_K$, the wave-length of the K absorption edge, it is necessary to correct the observed scattering factors for the effect of dispersion. According to Hönl's data, the dispersion correction has the value $-0{\cdot}66$; in other words, to obtain f for short waves from the experimental values for copper K_α radiation, 0·66 must be subtracted. The resultant values are given in column 8 of table 2.

§5. THEORETICAL SCATTERING FACTORS OF K^+ AND Cl^-

For spherically symmetrical atoms, f is related to the radial charge-distribution $U(r)$ by the equation,

$$f = \int_0^\infty U(r)\,\phi^{-1}\sin\phi\,dr,$$

where $\phi = 4\pi r(\sin\theta)/\lambda$. The charge distributions of Cl^- and K^+ were calculated by Hartree's method of self-consistent fields by Hartree$^{(4)}$ and by James and Brindley$^{(13)}$ respectively. These calculations have been subsequently repeated by Hartree$^{(5,6)}$ with considerably greater accuracy. In these calculations the effects of electron-exchange were neglected. Numerical calculations of atomic wave functions with allowance for electron-exchange were first made by Fock and

Petrashen⁽³⁾ for sodium, and by D. R. and W. Hartree⁽⁷,⁸⁾ for the normal and excited states of beryllium. They have since extended the work to Cl^-⁽⁹⁾, Cu^+⁽¹⁰⁾ and K^+. The results for K^+ have not yet been published and the writers are indebted to Prof. Hartree for permission to use them prior to their publication. In calculating the difference between the scattering factors corresponding to charge-distributions obtained with and without allowance for electron-exchange, it is more convenient and accurate to use the difference equation,

Table 2. Experimental results for potassium chloride

1	2	3	4	5	6	7	8
Spectra	sin θ/λ	I_r/A by experiment	f_T relative	f_T absolute copper K_α	e^M	f copper K_α	f $\lambda \to 0$
200	0·159	746·0	9·05	26·8	1·044	28·0	27·3$_5$
220	0·225	469·0	7·47	22·1	1·089	24·1	23·4$_5$
222	0·276	149·8	6·59	19·5	1·137	22·2	21·5$_5$
400	0·319	66·6	6·05	17·9	1·187	21·2$_5$	20·6
420	0·356	149·5	5·20	15·4	1·239	19·1	18·4$_5$
422	0·390	*100·0*	4·72	14·0	1·293	18·1	17·4$_5$
440	0·451	27·8	4·01	11·9	1·409	16·7$_5$	16·1
600, 442	0·478	56·1	3·69	10·9	1·471	16·0$_5$	15·4
620	0·504	39·4	3·46	10·2$_5$	1·535	15·7$_5$	15·1
622	0·528	35·5	3·18	9·4	1·602	15·0$_5$	14·4
640	0·574	33·8	2·80	8·3	1·746	14·5	13·8$_5$
642	0·596	71·1	2·60	7·7	1·822	14·0	13·3$_5$

Standardization data:

		f_T absolute	f_T relative	$\frac{f_T \text{ absolute}}{f_T \text{ relative}}$
Potassium chloride 420 compared with aluminium 220 gives	15·49	15·44	5·20	2·97
Potassium chloride 420 ,, aluminium 311 ,,	15·39			
Potassium chloride 422 ,, aluminium 220 ,,	14·01	13·96	4·72	2·95
Potassium chloride 422 ,, aluminium 311 ,,	13·91			

Mean value of f_T absolute/f_T relative, *2·96*.

$$f\,(\text{with exchange}) - f\,(\text{without exchange}) = \delta f$$

$$= \int_0^\infty \delta U\,(r)\,\phi^{-1}\sin\phi\,.\,dr.$$

The numerical results for f, with and without allowance for electron exchange, and δf for K^+, Cl^- and $(K^+ + Cl^-)$ are given in table 3. In the first column of the table, $(\sin\theta)/\lambda$ is expressed in terms of a_H, the radius of the one quantum orbit of hydrogen, and in the second column in angstroms, a_H being taken as 0·528 A. The results are shown graphically in figure 1, where f is plotted against $(\sin\theta)/\lambda$; the ordinates for δf are on a scale ten times larger than the ordinates of f.

Table 3. Theoretical scattering factors of K^+ and Cl^-

$(\sin\theta)/\lambda$		f_b, without electron-exchange			f_a, with electron-exchange			$\delta f = f_a - f_b$		
Atomic units	$Å^{-1}$	K^+	Cl^-	$K^+ + Cl^-$	K^+	Cl^-	$K^+ + Cl^-$	K^+	Cl^-	$K^+ + Cl^-$
0·0	0·000	18·00	18·00	36·00	18·00	18·00	36·00	0·000	0·000	0·000
0·05	0·095	16·61	15·43	32·04	16·77	15·85	32·62	0·160	0·420	0·580
0·10	0·189	13·70	11·84	25·54	14·03	12·30	26·33	0·333	0·455	0·788
0·15	0·284	10·97	9·57	20·54	11·31	9·79	21·10	0·341	0·219	0·560
0·20	0·379	9·15	8·27	17·42	9·35	8·35	17·70	0·200	0·081	0·281
0·25	0·474	8·03	7·49	15·52	8·11	7·53	15·64	0·084	0·044	0·128
0·30	0·568	7·30	6·74	14·04	7·34	6·79	14·13	0·044	0·054	0·098
0·35	0·663	6·70	6·09	12·79	6·73	6·16	12·89	0·031	0·071	0·102
0·40	0·758	6·14	5·44	11·58	6·18	5·53	11·71	0·039	0·086	0·125
0·50	0·947	5·08	4·21	9·29	5·15	4·32	9·47	0·075	0·108	0·183

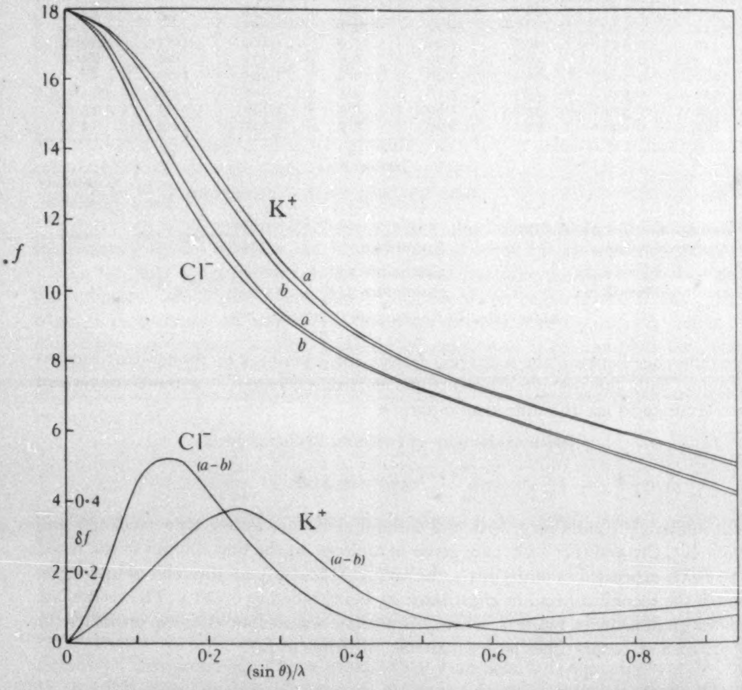


Figure 1. Atomic scattering factors of K^+ and Cl^- with and without allowance for electron-exchange; curves marked *a* are with exchange and curves marked *b* are without exchange. The ordinates of the difference curves, $a - b$, are increased ten times.

§ 6. COMPARISON OF EXPERIMENTAL AND THEORETICAL RESULTS FOR POTASSIUM CHLORIDE

The experimental values of *f* in the final column of table 2 are compared with the theoretical values in figure 2; the experimental values are shown by circles and the calculated values by full curves, the upper curve being the scattering factor with allowance for electron exchange. The agreement between the observed and calculated values is, on the whole, very close.

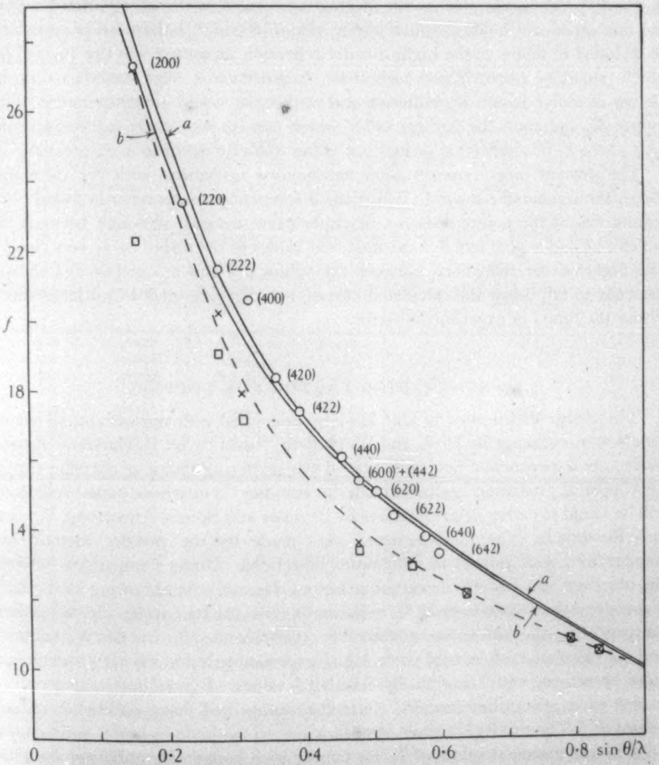


Figure 2. Comparison of experimental and calculated scattering factors for potassium chloride. The upper curve *a* is calculated with and the lower curve *b* without allowance for electron-exchange. Present experimental results are shown by circles; previous measurements by squares and crosses. The dashed curve is a mean curve through the earlier measurements shown by crosses

The previous measurements of James and Brindley[(13)] are shown up to a value 0·85 of $(\sin\theta)/\lambda$ by squares and crosses; the squares are the observed values without correction for extinction and the crosses are obtained after correcting for extinction. This correction was made by assuming the *calculated* value for the 200 reflection; the corrections for the other reflections were then obtained by applying a formula due to Darwin. Although the calculated curve with allowance for electron-exchange would give a slightly greater extinction correction, the increase is quite insufficient to account for the discrepancy between the observed and calculated values, particularly between the values 0·4 and 0·7 of $(\sin\theta)/\lambda$. In the region of the value 0·8 of $(\sin\theta)/\lambda$, the measurements are in good agreement with the calculated curves and this agreement holds to much higher values of $(\sin\theta)/\lambda$ than can conveniently be included in figure 2; the highest-order reflection measured was the 16, 0, 0 for which $(\sin\theta)/\lambda = 1{\cdot}276$. These high-order measurements were made possible by the use of molybdenum K_α radiation and working at liquid air temperature. With copper K_α radiation the highest order which can be accurately measured is the 6, 4, 2; the 8, 0, 0 reflection occurs but is too weak for accurate measurement.

The present measurements show satisfactory agreement with the calculated curves throughout the range in which the discrepancy was previously found. The general run of the points does not fit either curve exactly, although between the values 0·25 and 0·45 of $(\sin\theta)/\lambda$ the observed values fit the upper curve very closely. The higher-order reflections between the values 0·5 and 0·6 of $(\sin\theta)/\lambda$ show a tendency to fall below the calculated curves, but the difference is not large and is within the limits of experimental error.

§ 7. SCATTERING FACTOR FOR COPPER

The charge-distribution of Cu^+ has been calculated with and without allowance for electron-exchange by D. R. and W. Hartree[(10)] and by D. R. Hartree[(5)] respectively. An experimental determination of the scattering factor of metallic copper for copper K_α radiation has been made by Brindley[(1)], in whose paper references will be found to earlier determinations by Brindley and Spiers, Armstrong, Wyckoff and Rusterholz. The measurements were made by the powder method and standardized with respect to aluminium reflections. Direct comparison between the observed and calculated scattering factors was not possible owing to the large dispersion effect when copper K_α radiation is reflected by copper. It was shown, however, that the difference between the experimental f for copper K_α radiation and the calculated values valid when $\lambda \ll \lambda_K$ gave a mean value 2·6 of Δf, which is in close agreement with theoretically calculated values. It is of interest, therefore, to see what effect allowance for electron-exchange will have on the theoretical values of f. The results are given in table 4.

The experimental values of f_T for copper with copper K_α radiation are given in table 5. The temperature factor, e^M, is calculated from the characteristic temperature, which for copper is 315° K., by means of the usual Debye-Waller expression. The experimental values of f for copper K_α radiation are given in column 5 of table 5, and the corresponding theoretical values of f with allowance for electron-exchange and valid when $\lambda \ll \lambda_K$, are given in column 6 of the table; values of the difference, Δf, are given in column 7. The mean value of Δf, $3{\cdot}0_9$, is larger than the values 2·6 and 2·3 obtained theoretically by Hönl(11) and by Williams(15) respectively. Since the values of Δf in table 5 are the *differences* between the nearly equal values in columns 5 and 6, it follows that small errors in these values would have a relatively large effect on the Δf values, and in fact errors of the order of 1 per cent in the quantities f_T, e^M and the theoretical f values acting in the same direction would be sufficient to account for the apparently high values found for Δf. The agreement between the Δf values in table 5 and the directly calculated values of Hönl and Williams is probably as good as can reasonably be expected.

Table 4. Calculated scattering factors for Cu$^+$ with and without allowance for electron-exchange

$(\sin\theta)/\lambda$ (atomic units)	0·0	0·05	0·1	0·15	0·2	0·25	0·3	0·35	0·4
f, with exchange	28·00	26·84	23·95	20·48	17·16	14·40	12·12	10·35	9·08
f, without exchange	28·00	26·58	23·35	19·80	16·49	13·80	11·75	10·20	9·02

Table 5. Comparison of observed and calculated scattering factors for copper

Spectra	$(\sin\theta)/\lambda$	f_T (copper K_α)	e^M	f (copper K_α) measured	$f\,(\lambda \ll \lambda_K)$ calculated	Δf
111	0·241	$18{\cdot}3_7$	1·031	$18{\cdot}9_4$	$21{\cdot}9_5$	$3{\cdot}0_1$
200	0·278	$16{\cdot}5_5$	1·042	$17{\cdot}2_4$	$20{\cdot}6_0$	$3{\cdot}3_4$
220	0·393	$12{\cdot}4_5$	1·086	$13{\cdot}5_3$	$16{\cdot}6_0$	$3{\cdot}0_7$
311	0·461	$10{\cdot}2_7$	1·121	$11{\cdot}5_2$	$14{\cdot}6_0$	$3{\cdot}0_8$
222	0·481	$9{\cdot}5_1$	1·132	$10{\cdot}7_6$	$14{\cdot}0_5$	$3{\cdot}2_9$
331	0·605	$6{\cdot}9_3$	1·218	$8{\cdot}4_4$	$11{\cdot}3_2$	$2{\cdot}8_8$
420	0·621	$6{\cdot}5_1$	1·230	$8{\cdot}0_0$	$11{\cdot}0_0$	$3{\cdot}0_0$
					Mean	$3{\cdot}0_9$

§ 8. CONCLUSIONS

In these experiments we have been concerned primarily with tracing the origin of the discrepancies found when the intensities of X-ray reflections from powders are standardized with respect to reflections from aluminium and potassium chloride respectively. It is shown that whereas the scattering factors of aluminium obtained by the powder method agree closely with the single-crystal measurements of James, Brindley and Wood, and with theoretically calculated values, the scattering factors of potassium chloride obtained by the powder method differ from those measured on single crystals by James and Brindley. The difference occurs mainly in the region where the previous measurements showed marked disagreement with the theoretically calculated values; the present values are found to be in good agreement with the theoretical results. The discrepancies found in the powder method when potassium chloride and aluminium reflections are used as standards have arisen, therefore, through using the single-crystal measurements for potassium chloride as standard values.

The scattering factors of K^+, Cl^- and Cu^+ have been recalculated from the recent results of D. R. and W. Hartree for the wave functions of these ions obtained by the method of self-consistent fields with allowance for electron-exchange. It is shown that allowance for electron-exchange has only a small effect on the scattering factors, giving slightly higher values.

§ 9. ACKNOWLEDGEMENTS

We wish to thank Prof. Hartree, F.R.S., for kindly allowing us to use the results for K^+ calculated by himself and W. Hartree prior to their publication. We wish to thank also the Government Grants Committee for a grant with which part of the necessary apparatus was purchased, and Prof. Whiddington, F.R.S., for his interest in the work. One of us (P. R.) is also indebted to the Department of Scientific and Industrial Research for a maintenance grant.

REFERENCES

(1) Brindley, G. W. *Phil. Mag.* **21**, 778 (1936).
(2) Brindley, G. W. and Spiers, F. W. *Phil. Mag.* **20**, 865 (1935).
(3) Fock, V. and Petrashen. *Phys. Z. Sowjet.* **6**, 368 (1934).
(4) Hartree, D. R. *Proc. Camb. Phil. Soc.* **24**, 89 and 111 (1928).
(5) Hartree, D. R. *Proc. Roy. Soc.* A, **141**, 282 (1933).
(6) Hartree, D. R. *Proc. Roy. Soc.* A, **143**, 506 (1934).
(7) Hartree, D. R. and W. *Proc. Roy. Soc.* A, **150**, 9 (1935).
(8) Hartree, D. R. and W. *Proc. Roy. Soc.* A, **154**, 588 (1936).
(9) Hartree, D. R. and W. *Proc. Roy. Soc.* A, **156**, 45 (1936).
(10) Hartree, D. R. and W. *Proc. Roy. Soc.* A, **157**, 490 (1936).
(11) Hönl, H. *Ann. Phys., Lpz.*, **18**, 625 (1933).
(12) James, R. W. and Firth, E. M. *Proc. Roy. Soc.* A, **117**, 62 (1927).
(13) James, R. W. and Brindley, G. W. *Proc. Roy. Soc.* A, **121**, 155 (1928).
(14) James, R. W., Brindley, G. W. and Wood, R. G. *Proc. Roy. Soc.* A, **125**, 401 (1929).
(15) Williams, E. J. *Proc. Roy. Soc.* A, **143**, 358 (1934).

DISCUSSION

R. W. James: The paper appears largely to remove the discrepancies between the theoretical scattering factors for potassium chloride, and those measured by Dr Brindley and myself in 1928. At the date of the earlier experiments it seemed likely that some, if not all, of the lack of agreement would prove to be due to the approximations which had of necessity to be made in calculating the wave functions of K^+ and Cl^- by the method of the self-consistent field. Later work by D. R. Hartree and W. Hartree, in which allowance was made for electron-exchange, has shown that it is improbable that the discrepancies can be accounted for in that way. They are in fact almost certainly due to some systematic error in the earlier observations, probably connected with the use of large crystals as reflectors.

It will be seen that the observed results are always lower than the calculated ones, and the sources of error most likely to arise in the use of large crystals are such as to diminish the reflected intensities. The crystal faces had to be ground and this may have produced a non-crystalline layer which would act simply as an absorbing screen. The crystals of potassium chloride did in fact show a certain toughness and resistance to grinding which led us to suspect at the time the formation of such a layer, and the crystals were etched with water to remove it. This etching did as a rule appreciably increase the intensity, but the trouble may not have been entirely removed. Roughness on the surface, too, might act as a screen to considerable areas of the surface, particularly at oblique incidence. All such sources of error should become less important for the higher-order spectra, and this expectation again is supported by experiment.

It is satisfactory that this new work of Dr Brindley and Mr Ridley shows such good agreement between theory and experiment. The older experiments were done at a time when it was doubtful whether there was any agreement at all between theory and experiment in X-ray scattering. It showed that there was substantial agreement and so served its purpose at the time; but it is natural and satisfactory that improved experimental technique should give more reliable values.

Dr J. C. M. BRENTANO: I fully agree with the point stressed by the authors that the mixed powder method should not be applied indiscriminately to coarse particles. This point is so well established that the results of the experiments might almost have been foreseen, though this in no way detracts from their very great value in drawing attention to its importance in actual practice, when it is but too easily overlooked. The results of our respective experiences differ somewhat regarding the scope which can be given to the substitution method; the authors advocate it as a more general way for obtaining comparative values of scattering factors from coarse powders than appears warranted by our own findings. The point of difference arises essentially from this, that the elimination of the one particular error associated with the use of the mixed-powder method with coarse particles does not preclude a number of other less easily detectable errors associated not only with the numerical values of the absorption coefficients but also with the coarseness of the particles; a detailed investigation seems thus to be required for each individual powder. A fuller discussion is excluded from these comments. Reference may therefore be made to a paper in *Z. f. Phys.* **99**, 65 (1936) and to a joint paper by A. Baxter and myself, *Phil. Mag.* **24**, 473 (1937). These points are discussed in detail in a paper to be published in the next part of these *Proceedings*.

AUTHORS' reply. With regard to the statement that "the results of the experiments might almost have been foreseen", we consider that the question of the effect of coarse particles on intensities measured by the mixture method had not been adequately established, and that the results show what occurs in actual practice. Any theoretical analysis is only possible if very considerable simplification is introduced as to the size, shape and orientation of the particles. With regard to the other points raised by Dr Brentano, we look forward to his forthcoming publication in which he proposes to discuss them more fully.

THE NATURE OF FATIGUE* IN THE AUDITORY SYSTEM

By R. C. PARKER, Ph.D., Physics Department, University College, London

Received 15 *June* 1937. *Read in title* 26 *November* 1937

ABSTRACT. The ear is fatigued by a note of known frequency and known absolute intensity. The decrease in aural sensitiveness caused by exposure to this note is found by making a series of threshold measurements at short consecutive intervals after the cessation of the sound. The note used for threshold measurements is 410 c./sec., while for the fatiguing note both this frequency and others, within a range of 25 c./sec. to either side, are used, at two widely separated levels of intensity. When threshold determinations are made at the frequency of the fatiguing note, the duration of the auditory fatigue increases with the intensity of the fatiguing stimulus to attain rapidly a maximum value. At any frequency below or above that of the fatiguing note, the duration of the fatigue again increases with increase in the intensity of the fatiguing tone, but does so less quickly. The range of frequency over which auditory fatigue is apparent decreases as the intensity of the stimulus decreases. The results are shown to be consistent with the resonance theory of hearing.

§ 1. INTRODUCTION

DURING recent measurements on minimum audibility(1) certain supplementary phenomena were observed which seemed to be attributable to aural fatigue. Reference to literature revealed the paucity of fatigue data; much of the work ignored many necessary psychological conditions or else, satisfying these, failed to furnish sufficient information in regard to the power and purity of the fatiguing source. As an accurate and convenient method for measuring minimum audibility was to hand, the writer extended the method to the investigation of aural fatigue, bearing in mind both the general and particular conditions with which it was essential to comply.

§ 2. OUTLINE OF THE METHOD

The scope of the paper is confined to aural fatigue occasioned by exposing the ear to a pure tone of known intensity, and to the subsequent recovery. The behaviour of the ear was ascertained by measuring its threshold audibility at short intervals, both before and after the period of fatigue.

A possible criticism of the method is that the determinations of the threshold may themselves fatigue the ear, so that for the later values of the threshold there is the effect of an additional stimulus to be taken into account. The stimuli used in the threshold determinations are, however, very feeble and of very short duration, and so, as appears from the present work, are unlikely to cause additional fatigue. In further support of this it may be noted that threshold measurements made in quick succession in the absence of a preliminary fatiguing sound were sensibly equal from the beginning; see, for instance, figure 4.

---

* Throughout this paper the word "fatigue" has been used to describe the diminution of auditory sensitiveness which takes place when the ear is exposed to sound. Prof. Hartridge has, however, pointed out in a private communication that the effect is quite possibly not due to fatigue in the strict sense; for instance, it may be due to muscular contraction. The word is therefore used here merely as a convenient label for the effect.

To determine the threshold audibility use was made of a standard source which could be made to furnish sound of known absolute intensity, from zero upwards. To fatigue the ear an independent source, also of known intensity and frequency, was used. It was maintained for a period of 2 min. Four different frequencies of the fatiguing source were employed at two widely separated levels of intensity.

The conditions under which the experiment was performed were such as to eliminate, where possible, causes of distraction, i.e. in regard to the position of the observer and to the manner of signalling his response. Background noise was reduced to a minimum, and in cases where it affected the threshold audibility a correction was applied.

The investigations were carried out with thirteen observers.

§ 3. SOUND SOURCES

(*a*) *The standard source.* For the measurement of threshold loudness it is necessary to know the sound energy incident on the observer's ear. This was done by providing a standard source with a large baffle, so that radiations occurred as from a point source into a semi-infinite medium. The source used was that suggested by Prof. E. N. da C. Andrade in the *Discussion on Audition* held by the Physical Society in 1931. Air in a tube was maintained in vibration by means of a loud-speaker unit attached to one end: the other end was open and served as the source. The energy output was measured in absolute units, the power of the source being calibrated in terms of the electrical supply. A full account of this source has been given in a separate publication(1).

Throughout these investigations the frequency of the standard source was adjusted to a value of 410 c./sec., and to obviate detuning by temperature-change the tube was maintained at a constant temperature. The tone emitted by the source was practically free from harmonics and its intensity remained constant to within 1 per cent.

(*b*) *The fatiguing source.* It was not thought necessary to determine the power of the fatiguing source very precisely, for it would appear that its intensity would have to vary very appreciably before affecting the aural fatigue. Thus, an error up to 50 per cent was not considered serious.

The source consisted of a Rice-Kellog moving-coil loud-speaker mounted in the centre of a baffle board of 7-ply wood 3 × 2½ ft. and was operated by means of a suitable oscillator and amplifier. Its acoustical power was measured by matching its intensity with that of a note at the same frequency emitted by the standard source. A number of readings were taken at different intensities and a calibration was made in terms of the scale reading of a control potentiometer. After a little practice the desired accuracy was readily obtained.

The Rice-Kellog loud-speaker was finally mounted upon a wooden stand so that its centre was on a level with the observer's head and about 20 cm. from it. A wire framework, carrying a central ring, served as a point of reference for the observer's ear.

The fatiguing source was employed at levels corresponding to powers of 1000 and $3{\cdot}5 \times 10^6$ erg/cm.^{2}-sec. The intensity of the sound at the ear was 4×10^{-1} and 14×10^2 erg/cm.^{2}-sec. respectively. The latter value is below the threshold of feeling.

§ 4. DISPOSITION OF THE APPARATUS

The distribution of sound-intensity from a point source radiating into the half space is, in general, unknown when the presence of objects distorts the sound-field. In this experiment, where results are of a comparative character, such distortions do not matter provided that they are constant. Of greater consequence is irregular background noise, for this would distract the observer's attention and mask the variations which were being sought in the audibility threshold.

A situation in London was chosen. Measurements were made between the hours of 2 a.m. and 5 a.m. on Sunday mornings. The background noise was slight, and indeed on one occasion the main cause of distraction was the dripping of water from a drain pipe 30 m. distant. The measurements were made above an open courtyard which was surrounded by tall buildings, of which a section is shown in Andrade and Parker's paper(1), figure 13. The fatiguing source was placed edgewise on the parapet and was controlled from the transmitting-room.

It was first necessary to determine the minimum audibility. This was carried out as described in Andrade and Parker's paper. Six or seven readings were usually found to be sufficient. The fatiguing source had then to be switched on for 2 min. One minute before doing so, however, the operator rang the telephone bell once, and this warning enabled the observer to alter his position if he was feeling strained. A few seconds after the fatiguing source had been switched off the second series of minimum-audibility measurements was begun. This series was continued for 12 min. It is to be noted that the observer could see nothing of what was going on in the control room and had only his ear to guide him. It was found to be an advantage if, before making threshold measurements, the observer familiarized himself with the apparatus in the control room and also accustomed himself to recognize the frequency at which the standard source was used.

§ 5. RESULTS

Beginning with the fatiguing source at the low intensity, observations were carried out with three different values of the frequency-difference, i.e. the difference, in cycles per second, which exists between the frequency of the fatiguing source and the test note used for minimum audibility. It was found that (1) the fatigue was greatest when there was no frequency-difference, and (2) a value for the difference could be found at which there was no fatigue. With the fatiguing source at the high intensity, observations were made with four values of the frequency-difference.

For each setting of the fatiguing source observations were made by two or three observers, each observer taking three sets of readings. In figure 1 is shown the relation that was obtained between the threshold audibility and the time interval from the cessation of the fatiguing stimulus. From this curve may be seen the extent to which an observer's readings are in agreement. From figure 2 may be seen the spread of results among three observers. Both of these curves relate to the same setting of the fatiguing source. In table 1 are tabulated the values from which the curves in figure 1 were drawn. In the first column is given the time that has elapsed since the cessation of the fatiguing note, and in the second is shown the incident sound energy in decibels above true threshold. The true threshold was obtained from the minimum-audibility measurements immediately before each fatigue test. Average values for the r.m.s. pressure variations were, for the first three evenings, 1·30, 0·91 and 1·50 × 10^{-3} dyne/cm^2, values in good agreement with that previously given(1), i.e. 1·20 × 10^{-3} dyne/cm^2. On the fourth and subsequent evening a galvanometer of extended range was used and, as this was not calibrated in terms of the former current, absolute threshold values cannot be given.

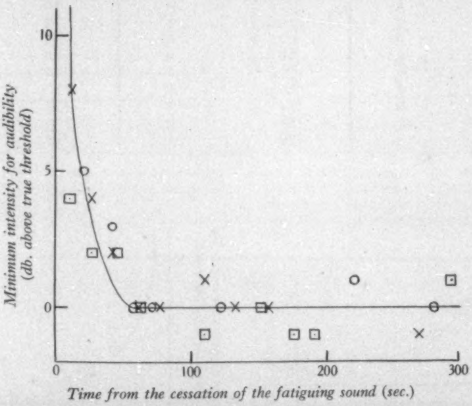


Figure 1. Intensity of fatiguing source, 1000 erg/cm^2-sec.; frequency of fatiguing source, 410 c./sec.; r.m.s. pressure-variation at true threshold, 1·30 dyne/cm^2. Observer A's first ⊡, second ×, and third ○ series of readings.

Figures 1 to 9 are experimental curves relating to the two levels of the fatiguing source and their associated frequency-difference. During the first few seconds the sensitivity of the ear recovers rapidly from a very low value. This initial state of low sensitivity usually lasts less than 20 sec., after which the ear regains, though more slowly, its initial sensitivity. The time taken for complete recovery is in the neighbourhood of 20 sec.

Table 1. The threshold of audibility subsequent to aural fatigue, for one observer. Frequency of the standard source, 410 c./sec.; frequency of the fatiguing source, 410 c./sec.; intensity of the fatiguing source, 1000 erg/cm^2-sec.

Time measured from the cessation of the fatiguing source (sec.)	Threshold of audibility (db. above true threshold)	Time measured from the cessation of the fatiguing source (sec.)	Threshold of audibility (db. above true threshold)	Time measured from the cessation of the fatiguing source (sec.)	Threshold of audibility (db. above true threshold)
20	5	11	8	10	4
40	3	26	4	25	2
56	0	42	2	43	2
70	0	60	0	60	0
120	0	76	0	110	−1
210	1	110	−1	150	0
280	0	132	0	175	−1
—	—	156	0	190	−1
—	—	270	−1	295	1

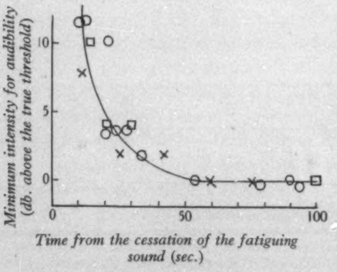


Figure 2. Intensity of the fatiguing source, 1000 erg/cm^2-sec.; frequency of the fatiguing source, 410 c./sec.; r.m.s. pressure-variation at true threshold, 1·30 dyne/cm^2. ○ Observer A; × observer B; □ observer C.

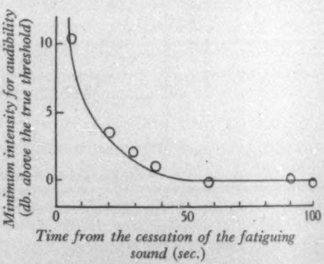


Figure 3. Intensity of the fatiguing source, 1000 erg/cm^2-sec.; frequency of the fatiguing source, 415 c./sec.

Consider first the results for the fatiguing stimulus of lower intensity, namely 4×10^{-1} erg/cm^2-sec. From figure 2, where the frequency-difference is zero, it may be seen that within approximately 10 sec. the energy required for audibility is only ten times the normal value. When the frequency-difference was increased to five, figure 3, the time required to attain this same value is approximately halved. The sensitivity of the ear is unaffected for the large frequency-difference of 15 c./sec., figure 4.

Figures 5 to 9 indicate the results obtained with the stimulating tone of higher intensity, i.e. 14×10^2 erg/cm^2-sec. Comparison between figure 2 and figure 5, which relate to zero frequency-difference, reveals the surprising fact that between these two cases there is no substantial difference in the nature of the resulting fatigue. When, however, we consider figures 6 and 7, which correspond to frequency-differences of 5 and 15 c./sec., we see that in contradiction to the effect previously noted, the fatigue has not sensibly diminished as compared with the case of zero frequency-difference. A slight diminution is apparent when the difference is 25 c./sec., figure 8.

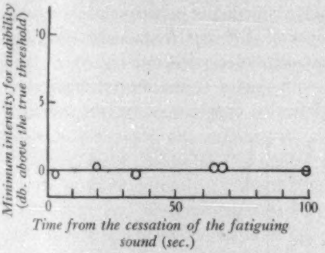


Figure 4. Intensity of the fatiguing source, 1000 erg/cm^2-sec.; frequency of the fatiguing source, 425 c./sec.

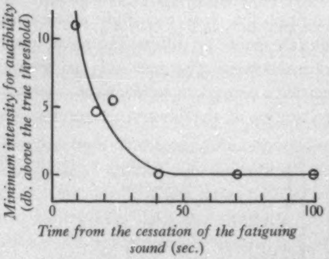


Figure 5. Intensity of the fatiguing source, $3{\cdot}5 \times 10$ erg/cm^2-sec.; frequency of the fatiguing source, 410 c./sec.; r.m.s. pressure-variation at the true threshold, 0·9 dyne/cm^2

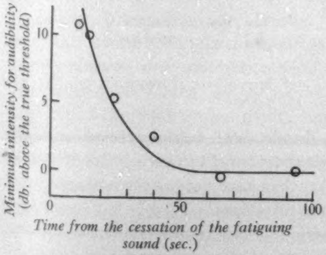


Figure 6. Intensity of the fatiguing source, $3{\cdot}5 \times 10^6$ erg/cm^2-sec.; frequency of the fatiguing source, 415 c./sec.; r.m.s. pressure-variation at the true threshold, 1·50 dyne/cm^2

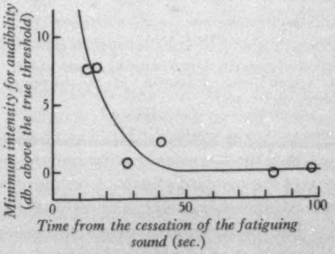


Figure 7. Intensity of the fatiguing source, $3{\cdot}5 \times 10^6$ erg/cm^2-sec.; frequency of the fatiguing source, 425 c./sec.

One observer showed in each measurement temporarily enhanced sensitivity, figure 9. His aural sensitivity rose to this level immediately on recovery and persisted for nearly 20 sec. Though measurements were extended over a twelve-minute interval no other observer showed this effect.

§6. CONCERNING THE OBSERVERS

The results obtained by the different observers, working without any possibility of being influenced by one another's figures, were found to be in much closer agreement than those generally recorded. Thus, the variation in mean minimum audibility for any particular evening did not exceed 50 per cent.

The thirteen observers who assisted in the measurements were, with one exception, familiar with sound experiments in a physical research laboratory. In addition five were, to a slight extent, musically trained, and consequently they were more capable of differentiating between tones of different frequencies than were the observers who had only an average acquaintance with musical tones. This capacity proved to be of great importance with regard to the reproducibility and reliability of the observer's results. The difficulty experienced by the untrained observer was marked. He was unable to decide, with any degree of certainty, whether the tone was pure or impure, or whether it was too high or too low to be that of the standard source. A feeling of futility then gave rise to a sense of annoyance and exasperation which adversely affected the responses.

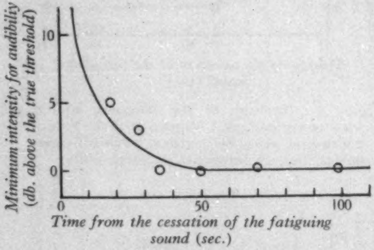


Figure 8. Intensity of the fatiguing source, 3·5 × 10^6 erg/cm²-sec.; frequency of the fatiguing source, 435 c./sec.

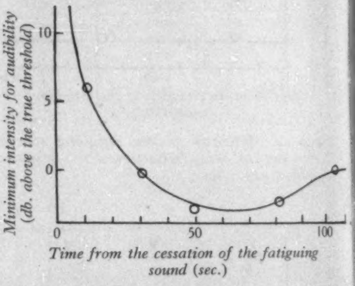


Figure 9. Intensity of the fatiguing source, 3·5 × 10^6 erg/cm²-sec.; frequency of the source, 435 c./sec.

The measurements extended over a period of six months and the thirteen observers showed a high degree of consistency. On two mornings the weather interfered with the experiment. On the first occasion the freshening of a light breeze into a gusty wind produced an irregular increase in the general noise-level. On the second occasion the observers suffered such discomfort from cold that they failed to make steady judgements. These two series were abandoned.

A tendency towards false responses, i.e. indications of a threshold measurement in the absence of a sound-field ⁽²⁾, was shown by observer B; he was more subject to this tendency during fatigue. The results of an observer's response were not communicated to him, though usually the observer's own judgement regarding his performance was found to be correct; when the results were not satisfactorily consistent he would report, without being asked, that he was not satisfied with his performance. The majority of observers only responded when aware of a definite aural sensation, but there were four who said that they were aware or sensed the note before hearing it.

§ 7. DISCUSSION OF RESULTS

Aural fatigue was first notice by Müller(3) in 1871 though subsequent experiments, extending to the year 1920, gave little positive evidence as to its nature. An historical survey for the period 1920 to 1927 has been compiled by Pattie(4), from which it is evident that the data, though more profuse and definite, express markedly divergent views. The first convincing investigations seem to have been made by Yoshii(5), Wittmaack(6) and Held and Kleinnecht(7), who showed, by visual after dissection, that only a limited region of the organ of Corti was affected when the ear was exposed to a pure tone for a sensible interval. It further appeared that whereas this region was confined between narrow limits for tones of low intensity, it became more diffuse as the intensity increased. A similar conclusion has been arrived at more recently by Davis, Laurie, and Stevens(8). They experimented on guinea-pigs and determined their electrical audiograms over the audible range, both before and after the walls of the cochlea had been pierced to destroy a finite portion of the organ of Corti. When the fatiguing tones were used at a level of 30 db. they noticed that the activated region considerably increased. Dworkin(9) employed this experimental lesion of the cochlea with cats and concluded against localization of low tones in the apex of the cochlea. It is not clear, from Dworkin's paper, at what levels he used the fatiguing tones or at what frequency.

Neither Wever, Bray, nor Horton(10, 11) were able to detect localization in the inner ear. Horton subjected a number of groups of guinea-pigs to notes at a frequency of 1000, 1500 and 3000 c./sec. for times varying from 100 to 1000 hr. and then tested their hearing by the method of conditioned response. Wever and Bray determined the audiograms of the same animals and concluded, as did Horton, that their aural sensitivity had been impaired more or less over the entire audible range. It is to be noted that the level of their fatiguing tone was 100 db. and this, as the authors themselves suggest, "may involve the entire extent of the basilar membrane and allied structures". Hughson and Thompson(12) similarly used the Wever-and-Bray technique but found no evidence for localization at low frequencies. Cats were the animals used in this instance. Bast, Eyster(13) and Culler(14) are representative of those who have extended the Wever-and-Bray technique. They found that localization definitely occurs, though they do not specify which particular part of the ear is involved. Davis and Derbyshire(15) have pursued a more exhaustive study of the Wever-and-Bray phenomena and have differentiated between the action potentials of the auditory nerve and the electrical response from the round window. They have discovered localization of sensitivity within the nerve, a fact which "supports a place-resonance theory of audition". Evidence from a different viewpoint comes from McCrady(16). In a study of the embryological development of the opossum he finds that, according to the human scale, five-sixths of the development in the embryology of the ear occurs after birth. This fact, coupled with a mammal's instinctive fear of noise, enabled him to record the ear's response along with its development. Notes were employed over the entire audible range and it appeared that whereas high notes were localized in the base of the cochlea, low notes were localized in the apex.

Involved in much of this work is an uncertainty as to which portion of the ear actually constitutes the hearing-mechanism. Guild(17), Bunch and Wolff(18) state that hearing is possible in absence of the organ of Corti. They tested the hearing of a number of patients with various aural conditions and correlated the results with post-mortem microscopical examinations of the ear. In a number of cases in which hearing was good, examination revealed complete atrophy of the organ of Corti. Hughson, Thompson(12), Bast and Eyster(13) also conclude that the integrity of the organ of Corti is not essential either for the Wever-Bray phenomena or for hearing.

It should be observed that all of the above instances which refute localization of low tones have involved intense fatiguing tones. Such cases may well be vitiated by reason of the presence of subjective harmonics which, for frequencies below 1000 c./sec., may be as intense as the fundamental.

Experiments of a more physical nature also have produced evidence as to the effect a loud note has upon the ear. Helmholtz(19), as far back as 1885, concluded that fatigue, which results from exposure to pure tones, extends over a finite frequency-difference. He gave the difference as approximately two tones. Measurements made by Flügel(20), indicated this difference to be roughly proportional to the minimum perceptible difference in frequency. A more exact measurement by Weinberg and Allen(21) gave it as 15 c./sec. Evidence for localization is also produced by Fletcher(22) who, when investigating the masking of one tone by another, shows the effect to be localized as regards frequency. Pattie(23), however, concluded that fatigue, induced by a tone of given frequency and intensity, affected the response of all tones subsequently used. He referred to the "non-specificity of fatigue". In general, however, it would seem safe to conclude that exposure to a pure tone fatigues the ear over a finite frequency-difference.

Among physiologists it seems agreed that the activated region of the inner ear increases in extent with increasing intensity of the fatiguing stimulus. Evidence on this point from physical experiments is conflicting. Flügel(20) concludes that fatigue resulting from exposure to pure tones is independent of the loudness, while Weinberg and Allen(21) suggest that fatiguing tones of low intensity may be the more effective in depressing the ear's sensitivity. Unfortunately neither they nor Flügel say how intense were their tones, though it is evident that neither covered an appreciable range. The possibility that an increase in the loudness of the fatiguing tone would cause greater fatigue is given by Pattie(23), who, using a Western Electric Company's audiometer, employed an intensity-range corresponding to 50 and 90 sensation units, the equivalent energy-ratio being approximately 3×10^4. An investigation along lines similar to those detailed in the present paper has been made by Ewing and Littler(24). They found that the intensity level of the fatiguing tone must reach a certain minimum before fatigue occurs. This level was 55 db. at a frequency of 250 c./sec. and 115 db. at 2048 c./sec. They arrived at no specific conclusion as to the extent of the fatigue, but found considerable differences among different observers. Unfortunately, with two exceptions (namely at 400 and 3000 c./sec.) the threshold values were determined at intervals of one octave, a fact conducive to error by reason of various resonances and subjective harmonics. The threshold note was adjustable in units of 5 db.

The investigation detailed in this paper leads to explicit evidence concerning the nature of auditory fatigue. It is concluded that as the intensity of the fatiguing tone is increased the auditory fatigue becomes apparent over a wider range of frequency. For the two intensitites of the fatiguing source used here, the magnitude of the fatigue remained independent of the loudness of the fatiguing source so long as its frequency, and that of the test note, were equal. However, during recent work on minimum audibility, auditory fatigue of a small magnitude was occasioned by tones of very low intensity, namely 2 db. It would thus seem that the magnitude of the fatigue increases with the loudness of the fatiguing tone till it rapidly attains a maximum value, and there remains steady until the threshold of painful loudness is reached. When the frequency of the two sources differ, and the intensity of the fatiguing source is increased, there is no fatigue until the intensity attains a certain minimum value, thereafter the magnitude of the fatigue increases to a maximum value.

These results are interesting in so far as they may be related with existing theories of audition. One or other of two theories, the telephone and the resonance theory, is now generally accepted; their merits have been recently discussed by Kagen(25) in accordance with existing data. The theory of resonance, first clearly postulated by Helmholtz, postulates that resonance in the region of the basilar membrane results in stimulation of the nerve terminals over a finite section, the particular part of the membrane involved depending upon the frequency of the stimulus. Wegel and Lane(26), in an experiment concerned with the masking of pure tones, obtained a hypothetical curve of vibration for the basilar membrane. This indicates that the extent of the stimulated region increases with the intensity of the stimulus. Now, as only those nerve endings which are stimulated would suffer fatigue, these theories at once suggest that, though localized, auditory fatigue resulting from exposure to a pure tone would increase in extent with increase in the intensity of the stimulus. Further, there would be no fatigue provided that the frequency of the testing note, and the frequency of the stimulating tone, differed by a large interval and was not harmonically related. The results are, then, consistent with the resonance theory of audition. Moreover, the fact that the magnitude of the auditory fatigue increases with the intensity of the fatiguing stimulus up to a certain point, suggests that the mechanism depends in some way upon the amplitude of stimulation of the nerve endings. In particular, there would be a minimum amplitude of motion of the basilar membrane at which full fatigue occurs.

§ 8. ACKNOWLEDGEMENTS

In conclusion I wish to express my indebtedness to Prof. E. N. da C. Andrade, F.R.S., at whose suggestion the investigations were made, for his continued interest and encouragement and for the experimental facilities placed at my disposal. My thanks are also due to Prof. D. M. S. Watson, F.R.S., for placing a room in his department at my disposition, and to the friends who helped me in making the tests.

REFERENCES

(1) Andrade, E. N. da C. and Parker, R. C. *Proc. roy. Soc.* A, **159**, 507 (1937).
(2) Smith, E. M. and Bartlett, F. C. *Brit. J. Psychol.* **10**, 164 (1919).
(3) Müller, J. J. *Ber. sachs. Ges.* (*Akad.*) *Wiss.* **23**, 115 (1871).
(4) Pattie, F. A. *Amer. J. Psychol.* **38**, 39 (1927).
(5) Yoshii, U. *Arch. Ohr.-, Nas.-, u. KehlkHeilk.* 1914; *Z. Ohrenheilk.* **58**, 201 (1909).
(6) Wittmaack, K. *Pflüg. Arch. ges. Physiol.* **120**, 249 (1907); *Z. Ohrenheilk.* **54**, 37 (1907).
(7) Held, H. and Kleinknecht, F. *Pflüg. Arch. ges. Physiol.* **216**, 1 (1927).
(8) Davis, H., Laurie, M. H. and Stevens, S. S. *Ann. Otol., etc., St Louis,* **44**, 776 (1935).
(9) Dworkin, S. *Ann. Otol., etc., St Louis,* **44**, 807 (1935).
(10) Wever, E. G., Bray, C. W. and Horton, G. P. *Ann. Otol., etc., St Louis,* **44**, 772 (1935).
(11) Horton, G. P. *J. comp. Psychol.* **18**, 405 (1934).
(12) Hughson, W. and Thompson, E. *Ann. Otol., etc., St Louis,* **44**, 786 (1935).
(13) Bast, T. H. and Eyster, J. A. E. *Ann. Otol., etc., St Louis,* **44**, 792 (1935).
(14) Culler, E. A. *Ann. Otol., etc., St Louis,* **44**, 809 (1935).
(15) Davis and Derbyshire. *Amer. J. Psychol.* **113**, 476 (1935).
(16) McCrady, E. *Ann. Otol., etc., St Louis,* **44**, 813 (1935).
(17) Guild, S. R. *Ann. Otol., etc., St Louis,* **44**, 738 (1935).
(18) Bunch, C. C. and Wolff, D. *Ann. Otol., etc., St Louis,* **44**, 754 (1935).
(19) von Helmholtz, H. *Sensations of Tone*, p. 418 (Eng. trans.).
(20) Flügel, J. C. *Brit. J. Psychol.* **11**, 105 (1920).
(21) Weinberg, M. and Allen, F. *Phil. Mag.* **47**, 126 (1924).
(22) Fletcher, H. *Speech and Hearing* (London, 1929).
(23) Pattie, F. A. *Amer. J. Psychol.* **38**, 39 (1927).
(24) Ewing, A. W. G. and Littler, T. S. *Brit. J. Psychol.* **25**, 284 (1935).
(25) Kagen, S. *Rev. Acoust.* **4**, 130 (1935).
(26) Wegel, R. L. and Lane, C. E. *Phys. Rev.* **23**, 266 (1924).

THE APPRAISEMENT OF LIGHTING

The twenty-second Guthrie Lecture, delivered on 22 October 1937 *by*

C. C. PATERSON, O.B.E., D.Sc., M.I.E.E., F.Inst.P.

§ 1. HISTORICAL

In the archives of one of our Ancient City Guilds, the Worshipful Company of Tallow Chandlers, we have an early document of 1680 bearing upon the official appraisement of lighting—in this case the public lighting of the City of London. It takes but a minute to read a few extracts from this very human document—an appeal to the Court of Common Council of the City of London by the Craft of the Tallow Chandlers. These craftsmen had already for two and a half centuries enjoyed a practical monopoly of the field of artificial lighting, for tallow candles had been the recognized means of artificial lighting with hardly a rival since before the coming of the Conqueror. The makers of tallow candles were suddenly faced with a rival luminant—or as they charmingly called it, lucidary—the oil lamp.

This is the substance of their petition:

> REASONS humbly offered to the......Lord Mayor, Aldermen, and Commons of the City of London........by the Worshipful Company of Tallow Chandlers against Setting up and establishing the Lamplights of any sort in this City, as varying from the antient custom.
>
> THAT this Company have been Incorporated about 230 years...... and have always assisted as well in Purse as Person to add to its Grandure, and to the support of the present Government.
>
> That this Company, with the whole City.....thought themselves safe from any other invasion of their Laws, one of which is an Act of Common Council, made the 3. of October 1599, whereby every Householder from the first of October to the first of March in every year for ever, should cause a substantial Lanthorn and a Candle of Eight in the Pound to be hanged without their Doors.
>
> That notwithstanding the said Act (still in force) certain unfree Men, who are not capable of serving any office in any Company, nor Office of Trust within this City.......have set up, and do continue in the Streets of this City..........a great number of *Convex-Lamps* and other *Lucidaries*, in opposition to, and derogation of, the said Act, and to the manifest Injury of this and other Companies, in their lawful Trades.
>
> That the setting up, and use of the said *Lamps*.....will be a great Prejudice:
>
> First, to this Company, in taking away the Use of their lawful trade....and that if the continuance of these lamps be suffered, they will hinder the making and selling of Seventeen Dozen of Candles to every Lamp set up and used in this City....in every Year....

> And although great annual Rents, and other Considerations may be offered to this City by the Partners of the several New Lights, (and as they pretend) towards payment of the Orphans, yet nevertheless it's hoped, that not any of those New Lights will be Established for the sake of such Rents; and at the same time, by so doing, deprive the Tallow-Chandlers, and other Trades in the Profits thereof, to a far greater value than the Profits of the Lamps can accrue unto the Orphans.
>
> And to other Trades, as the Horners in making of Leaves for Lanthorns for burning Candles in; Tinmen and Spinners of Cotton, whereof the Twentieth part is not nor cannot be used in Lamps, which is, and must be in Candles; and must necessarily deprive many Hundreds of Persons, (that live solely by those Trades), of their Maintenance and Livelyhood.
>
> It is humbly hoped that the Act of *Common Council* for enlightening the Streets of this City with Candles in Lanthorns may be strictly observed, or that this Honourable Court will be pleased to make another Act, for the more strict and regular Observance of the Duty of Lighting the Streets of this City.......with Tallow Candles in Lanthorns, which will be cheaper to the Inhabitants than any sort of Lamps.

You will notice that each householder was from 1 October to 1 March in every year *for ever* to cause a substantial lanthorn and a candle of eight to the pound to be hanged without their doors. There is still something to be said for the method these pioneers used for appraising their light. Being at that age uncontaminated by the conceptions of physics, they resisted the temptation to specify *light* and insisted with touching reiteration on the two tangible things they knew—the tallow candle and the lanthorn. This simple and commonsense principle of appraising lighting by boldly specifying the lamps which radiate the light is probably still the most widely used in common practice.

§2. OBJECT OF LECTURE

I am apprehensive lest this talk should degenerate into a mere lecture on photometry, and an indifferent one at that. For my object is wider. It is rather to review some of the many and varied circumstances in which one characteristic or another of light must be estimated in relation to the purpose for which the light is required. Nevertheless, the measurement of light by physical or physiological means is in fact the inevitable background of my subject.

The essential motive in the inception of the Physical Society was the study of experimental physical methods. I need make no excuse this evening therefore if I centre my discourse round various techniques which have been evolved by the physicist and the engineer for the better study of the art of using light. The contributions of the physiologist are at least as important. Certain techniques can be considered to be as much within the sphere of one as of the other, but my point of view and terminology will, I admit, not be that of the physiologist, although

I hope that nothing I say will be at variance with a sound physiological standpoint.

When I joined the National Physical Laboratory some 35 years ago with the task of evaluating and rendering as reproducible as possible the unit of luminous intensity, i.e. the candle, few people thought of the value of light to the community in terms of anything but intensity. This was unfortunate, but perhaps natural, because the intensity of a source of light was the one quality which could be readily measured. Furthermore, the idea was simple enough for engineers to understand.

The measurement of brightness, of total flux, of colour, of contrasts, of the disturbing effect of unwanted light, the differences between normal eyes, and such like—measurements of all these quantities had yet to come. Some of the techniques for them are still very imperfect; but realizing the importance of the effects for practica llighting, workers are now having to seek techniques for appraising even the most elusive of them.

In some of these techniques matters have been much complicated by the appearance of new lamps which yield light of the most varied colours. The appraisement of lighting effects was difficult enough when our lamps emitted approximately white light, i.e. light which can be matched in its hue with that from a black body at some temperature or another. But now that so many lamps emit merely a line spectrum of some gas or vapour, our technique must no longer assume (as it used to do) that the light emitted approximates to that of a continuous spectrum.

§3. LUMINOUS INTENSITY

(*a*) *Visual techniques*. In the early years of the century our carbon-filament substandard lamps had hardly been established before the operating temperatures of incandescent lamps began to climb. The Nernst lamp, then Tantalum, Osmium and Tungsten appeared, bringing with them disturbing changes in the hue of the light.

It was fortunate that there were good physicists at that time who foresaw that alongside the effort to evaluate such higher-temperature sources by the old methods of direct photometric comparison, a sounder and more fundamental technique must be established, based on spectrophotometric methods. The Americans undertook several very laborious investigations to determine the relative luminosity curve, figure 1, for the average human eye—the type of curve which was, I believe, first produced by Sir William Abney. From 1912 to 1922 curves were obtained for about 250 observers, and as a result (and also because the results of measurements on a group of Japanese observers showed no sensible racial disagreement, such as was at one time suspected), the average curve, figure 2, was internationally agreed. But it does not do to forget that this average curve has as its origin the diagram shown in figure 1, in which we observe the very great spread which prevails amongst normal individuals.

To allow for the deviation of individuals from the average colour-sensitivity, a system, due to Ives, has been evolved for determining, by a simple test, the extent of the departures of individual observers from "average vision", so that an appropriate correction can be made to photometric observations in which a colour difference is present. This is a partially successful device only, but on the whole we are better off with than without it. Briefly, the test consists in determining for any observer the ratio of the transmissions of specified yellow and blue filter solutions, with a Guild flicker photometer at a high field brightness, 2·5 equivalent ft. candles, in order to ensure that the test shall apply to foveal vision. Normal observers' yellow/blue ratios range over a spread of about ± 15 per cent from the mean. If these Y/B ratios are plotted against the individual observer's candle-power or lumen determinations in the presence of a colour difference, the slope of the best straight line through the observations is determined by the extent and form of the

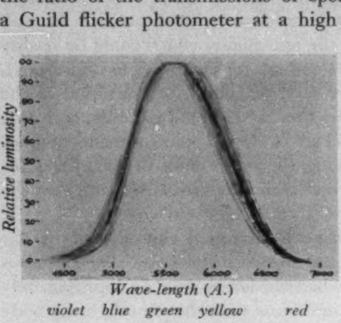


Figure 1. Curves of relative luminosity for 125 persons.

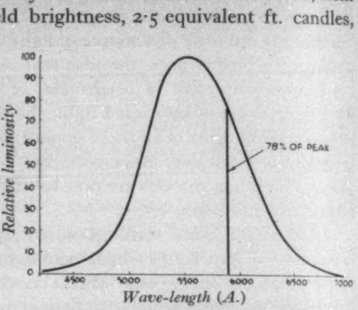


Figure 2. Curve of average relative luminosity, adopted internationally.

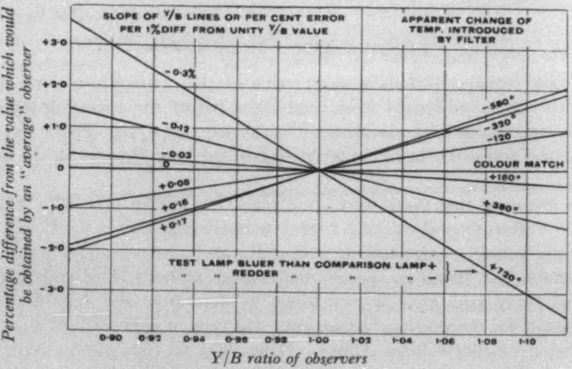


Figure 3. Lines relating Y/B of observers in the comparison of light sources operating at different colour temperatures.

colour difference. For example, if we photometer carbon or tungsten filament light sources operating at different colour temperatures, and plot the results against the *Y*/*B*s of the observers, we obtain a family of curves having different slopes, figure 3. If we then plot the slopes of these curves against the difference in temperature between the light sources compared, we obtain a straight-line relationship, figure 4, from which we can determine the slope of the *Y*/*B* line for any difference of colour-temperatures. Therefore when photometering tungsten or carbon filament lamps, we can, if necessary, make a suitable correction to any individual observer's results provided we know the extent and direction of the colour-temperature difference and the observer's *Y*/*B* ratio.

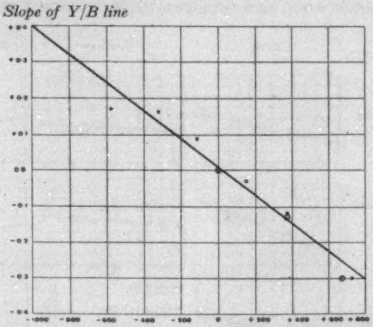


Figure 4. Relation between slope of *Y*/*B* lines and the colour-temperature differences between the sources compared.

This method is only of limited application when continuous-radiation sources are to be compared with sources emitting line or band spectra. This will be appreciated by reference to the diagrams, figure 5, where the results of photometric comparisons between tungsten and neon, sodium, and high-pressure mercury sources have been plotted against the *Y*/*B*s of the observers(1) using different forms of photometer head. We see that in some cases the "spread" from the best line through the observations is very great, and in many cases is of the same order of magnitude as the correction which the slope of the line would indicate to be necessary.

It will be seen, therefore, that Ives's proposal is mainly applicable for comparing light sources in which the radiation is continuous and approximates to that of a black body.

Having thus, through the relative-luminosity curve, obtained a value for the luminosity at each wave-length, we can now interpret the spectrophotometric readings on a coloured source of light in terms of the intensity-value of such a source for human vision. It is obvious that the appraisement of light by this technique is easier for radiators with a continuous spectrum than for those with line spectra. The latter cannot in fact readily be measured spectrophotometrically. It is usual in such work to find a colour filter which, when put in front of a tungsten filament standard lamp of appropriate temperature, will give a colour match (though not an energy match) with the line-spectrum source to be determined. The filter is then measured spectrophotometrically for its absorption, so becoming a standard "colour converter" whose constants are known.

It may be interesting to demonstrate how closely we can approximate, with filters used with filament lamps, to the colour of certain vapour lamps now in common use for public lighting. [To illustrate the description which follows, images of the various photometer fields mentioned were thrown on the screen.]

You will remember how comparatively easy it is to balance a Lummer-Brodhun photometer with a large field (6 to 8 degrees) when there is no colour difference present—as for instance when two tungsten-filament lamps operating at the same colour temperature are being compared. We will attempt to show, by means of superposed projections, the appearance of different photometer fields when heterochromatic comparisons are being made.

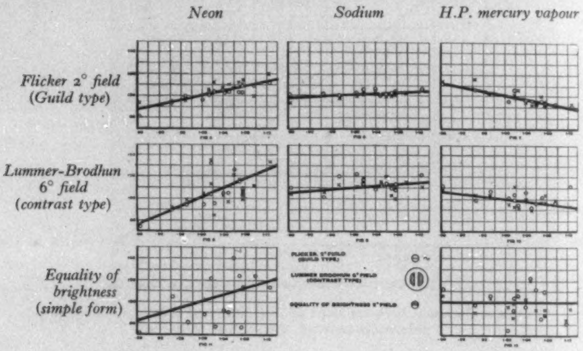
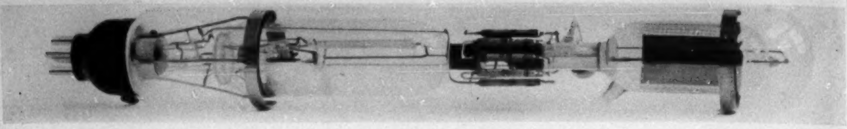


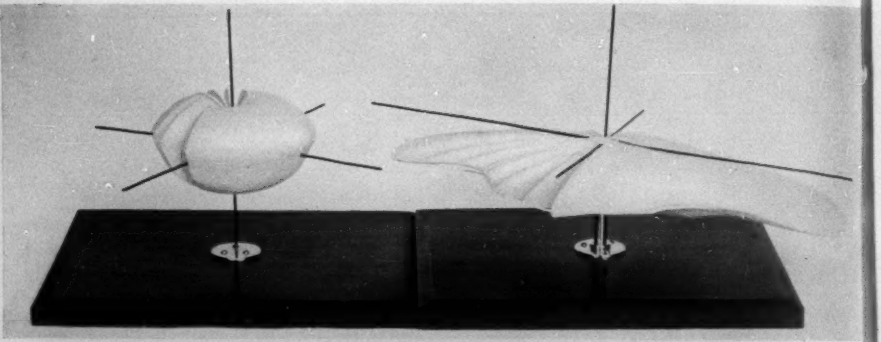
Figure 5. Representative Y/B curves obtained when comparing electric discharge lamps with incandescent tungsten.

First the 6-degree large Lummer-Brodhun field; we can see, as the brightness of the adjacent fields is adjusted, how difficult it is to balance with the full colour difference between tungsten and high-pressure mercury light. This colour difference can be minimized by means of a suitable blue filter in front of the tungsten source, and you will see now how much easier it is to determine the point of photometric balance as the brightness is adjusted. For the best work a smaller field should be used in order to restrict it to foveal vision. Here is such a small 2-degree equality of brightness photometer with the full colour difference tungsten to high-pressure mercury. And next we see it with the filter in front of the tungsten source to give minimum colour difference.

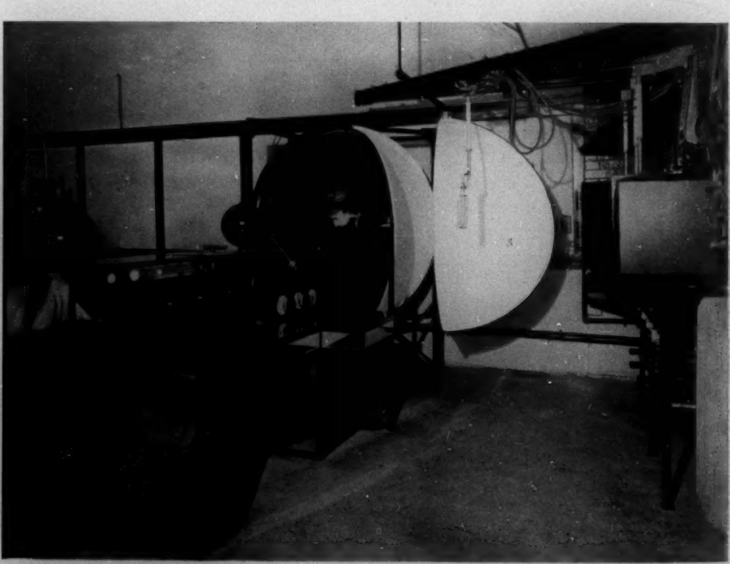
We will now project alternately on to the same portion of the screen, a small circular (2-degree) field from the tungsten and high-pressure mercury sources,



(*a*) Valve photocell unit.



(*b*) Models of polar distribution surfaces.



(*c*) Integrating photoelectric photometer for measuring tungsten-filament electric discharge lamps.

respectively. This simulates the conditions in a flicker photometer, such as the Guild photometer, except that in the latter a 25-degree steady white surround field is used to increase the comfort of balancing. The photometric balance in this case is of course indicated by the setting position at which flicker disappears. This we see is fairly easy to determine, even though the full colour difference is present as in this case. Why then use any other photometer than the flicker for heterochromatic comparisons? There is a drawback of course. The flicker photometer must be operated under carefully prescribed conditions and is very tiring to use continuously. It is thus unsuitable for making routine day-to-day measurements. Even with carefully chosen filters and yellow-and-blue-corrected human individuals, the measurement of the intensity of differently coloured modern lamps is liable to considerable uncertainty. So you see it is all rather artificial. We are trying to make of the human eye as accurate and reproducible a measuring-instrument as we can. But when we have done all the things I have just described, I am not sure how justifiable is the claim that we are basing our appraisements of light on the judgements of human vision.

(*b*) *Photoelectric techniques*. Having consented to this measure of arbitrariness, our critics will hardly complain if we seek the assistance of the photoelectric cell to replace the eye and to relieve it of the tedious and exacting discriminations which this photometric work involves. The photocell of course has its own traps for the unwary, which are both optical and electrical in character. In the case of photocells of the Elster-Geitel type, which are still found to be most suitable for high-precision measurements, the chief electrical uncertainties are surmounted by housing the photocell complete with amplifying valve and grid leak in an evacuated glass envelope, as shown at (*a*) in plate I. By this means instability due to variable surface leakage is avoided, and the highly insulated lead from photocell to valve is kept extremely short. This enables the unit, together with its associated components, to be efficiently screened from external electrical disturbances.

Other causes of uncertainty in such photoelectric apparatus may arise from (*a*) the temperature coefficient of the photocell, (*b*) fatigue, and, in cells of bad quality, (*c*) departure from linearity of response. Moreover, where it is required to make illumination measurements, errors may occur as a result of departure from true cosine response, and of course from the fidelity with which the relative-luminosity curve of the cell corresponds with that of the average human eye. No cell as yet approaches sufficiently near the required distribution, but Preston at the National Physical Laboratory has studied light-filters for use with a certain thin-film potassium photocell, and has produced the high degree of coincidence shown in figure 6 with a loss of sensitivity of about 75 per cent for tungsten radiation and about 80 per cent for high-pressure mercury lamps. But such a loss does not matter when we can have practically as much amplification as we choose. Thus, you see, by using a photocell with a carefully designed filter and a substandard lamp, we can approximate to the response of the limited region at the centre of the fovea of the average human eye, and so obtain a consistent measure of the intensity of our coloured sources of light.

In general the Elster-Geitel type of photocell is chosen for precision measurements, because of the higher stability available in special types and of the fact that it is a high impedance device and therefore the photoelectric current can readily be amplified. However, the selenium rectifier type of photocell is gaining popularity for industrial photometric purposes because of its simplicity. This type of cell is a low-resistance device which can be connected direct to a low-resistance micro-ammeter of 50 to 100 ohms, the indications of which will be closely proportional to the incident light. Fortunately, the spectral sensitivity of these cells, figure 7, although it departs by an appreciable amount from the "average visibility curve", is a sufficiently close approximation to enable the light-output or illumination from incandescent tungsten sources, over the normal range of operating temperatures, to be compared to an accuracy of the order of 5 per cent. Colour filters have also been proposed and made for use with this class of cell so that it may be used for comparing coloured light sources. But the absorption of such filters is necessarily high if accurate correction to "average eye sensitivity" is required, and amplification is not possible owing to the low resistance of the cell, so that the application is strictly limited.

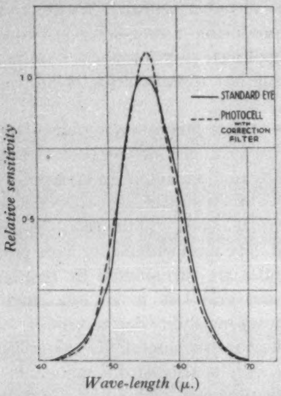


Figure 6. Relative spectral sensitivity of photocell with correction filter to give average-eye response.

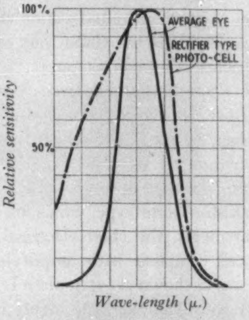


Figure 7. Relative spectral sensitivity of photocell of rectifier type, and of average eye.

Even though some may be inclined to be critical of all these artificial aids to absolute accuracy, there is no doubt about the extraordinary sensitivity obtainable by the use of the photocell in photometry. I speak of sensitivity, not of absolute accuracy, and for many purposes sensitivity is more important than absolute accuracy.

[The lecturer then showed a photometer and control gear which employs a photocell for appraising the intensity of the light falling on it. The galvanometer was shown to give a deflection of about 3 ft. for a change of $\frac{1}{2}$ per cent in the light falling on the cell. The apparatus incorporates one of the composite vacuum units referred to earlier in the lecture, the electrical amplifier circuit being effectively screened. Actually the unit used in this photometer is fitted with a grid leak of approximately 10^{11} ohms, giving maximum detectable sensitivity to light of 10^{-9} lumens. This is reduced to 10^{-7} when the apparatus is used with the galvanometer incorporated in the control cabinet.]

The photoelectric photometer is an exceedingly useful technical device and a tribute to those who have brought it to such a state of refinement. But it does not concern us or assist us very much in the broader aspects of the appraisement of lighting.

There is one application which demonstrates very well the convenience of the selenium rectifier photocell in an industrial laboratory. Polar curves of lighting fittings—or may we call them "lucidaries"?—are tedious to take and to plot. This is particularly so with many modern types of which the polar curve is not a figure of rotation but is designed to be asymmetric, in order, for instance, to throw more light up and down a street than across it, figure 8. In order to define them, such lucidaries require a considerable number of polar curves taken in different planes through their vertical axes, which is all exceedingly tedious. Two solid polar graphs are shown at (*b*); plate I

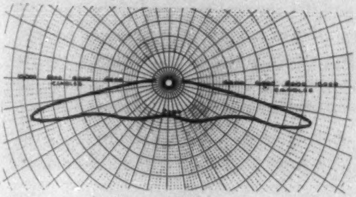


Figure 8. Polar distribution curve of asymmetric refracting lighting fitting.

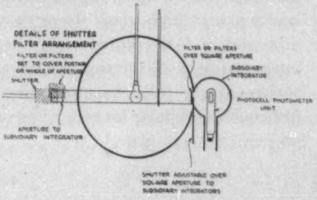

DETAILS OF SHUTTER
FILTER ARRANGEMENT
FILTER OR FILTERS
SET TO COVER PORTION
OR WHOLE OF APERTURE
SHUTTER
APERTURE TO
SUBSIDIARY INTEGRATOR
FILTER OR FILTERS
OVER SQUARE APERTURE
SUBSIDIARY
INTEGRATOR
PHOTOCELL PHOTOMETER
UNIT
SHUTTER ADJUSTABLE OVER
SQUARE APERTURE TO
SUBSIDIARY INTEGRATORS

Figure 9. Diagrammatic arrangement of integrators of photoelectric photometer.

[A device was then demonstrated in which a photocell rapidly explores and records the light-intensity in one plane after another, enabling the work to be done expeditiously. The only skill required is that of the operator who must faithfully follow the vagaries of the track of the spot of light on the polar chart.]

There is now a high probability that the accepted standard of luminous intensity will no longer, as heretofore, be a pentane lamp nor a Hefner lamp, nor tungsten lamps calibrated in terms of these, nor even, as defined by Act of Parliament, a "sperm candle weighing 8 to the pound". But that one square centimetre of black body at the freezing point of platinum will be assigned the value of exactly 60 candles. Such a standard, though arbitrary, leaves the value of our present unit practically unaltered, and will always be reproducible. It has in fact been already reproduced within an accuracy of approximately 0·2 per cent at the Bureau of Standards, Washington, and at the National Physical Laboratory, averages of series of some 30 sets of determinations being used.

(*c*) *Total flux.* Before we pass from the measurement of intensity we ought to note the technique for obtaining a measure of the total flux of light from a source, or in other words its average intensity. The principle of the Ulbricht sphere is simple and attractive, but it is anything but simple to ensure that the magnitude of the unit of intensity of a standard in a single direction is accurately reproduced in the mean intensity in all directions of any given source. A diffusing, truly white surface is required. It is easy to measure the mean intensity of a source in all directions and make a standard of it for calibrating the Ulbricht sphere. But unless the light from the source ultimately to be measured has exactly the same hue as the light from the standard, errors may creep in. These errors can be of the order of 1 to 2 per cent, with line sources, even when using the accepted white paints available for coating the sphere interiors.

If a photocell is used as a detector with an Ulbricht sphere, it may sometimes conveniently be placed in a subsidiary integrator, figure 11. The window between the main and the subsidiary integrators is occupied by a shutter and appropriate colour filters which adjust the sensitivity and the spectral response of the photocell unit; and as, furthermore, when filters are used in this way, the photocell receives integrated light, the arrangement avoids any inaccuracy, due to variations over the surface of the cell. An integrating photoelectric photometer incorporating this principle and suitable for measuring tungsten filament and electric discharge lamps(2) is shown at (*c*) in plate I.

§4. GLARE

Glare. Now these elaborate techniques which we have been reviewing, and all the other refinements which on account of time I have not been able to touch upon, concern merely the appraisement of intensity. But the appraisement of light for seeing purposes depends but remotely on the intensity of sources of light. In fact I think we must agree that to the ordinary man, in his seeing processes, intensity is really but an abstract magnitude, except in one respect: the disturbance of vision owing to the presence of bright sources of light is due primarily to the intensity of such sources. From this point of view, therefore, intensity may perhaps remain of importance as a practical magnitude. This phenomenon of glare has been investigated very carefully during the past few years(3, 4). Glare is encountered in one of its most exaggerated forms in our roads at night, where the two classes of glare are well exemplified. The first is disability glare illustrated by the motor headlight; here vision of objects is to a large extent paralysed by the glaring effect of such lights. The second is discomfort glare illustrated by street-lighting lamps which appear to be close to the objects that one desires to see. Such street lamps are sometimes bright enough in relation to their surroundings to cause a certain measure of disability glare; that is to say visibility is actually improved if the eyes are shaded from the direct light of the lamps. But Stiles's results show that as a rule these street lamps which appear in the field of view do not embarrass the eye in its discrimination of objects; their deleterious effect is limited to causing a sense of discomfort. This probably depends on the intensity and brightness of the source, the nearness of its image on the retina to the fovea, and the darkness of the background of the general field of view in which such lights are located. I find there is a good deal of confusion of thought on this subject owing to a tendency to jump to the conclusion that when someone is conscious of discomfort glare, visibility is necessarily impaired. I have noticed, furthermore, a considerable difference in the sensitivity of individuals to discomfort glare.

Stiles has shown how the disability effect of glare for any set of conditions can be calculated from laboratory data, and has established much of the mechanism of disability glare; but in some problems practical conditions are so complex as to make the calculation uncertain and tedious, and in some points the gap between laboratory and practical conditions has yet to be bridged. For example, when your field of view, instead of being a uniformly bright area as in laboratory work, is an area of very varying brightness, and glare sources are scattered in it in positions which depend upon the layout of a considerable length of road, it is obvious that the collection of the essential data alone is a considerable task, and their interpretation is by no means either simple or certain. The very nature of the problem has made difficult the construction of a simple field instrument for measuring glare directly which is suitable for engineers to use, although one very ingenious field instrument was made and tried. We have also no way as yet of measuring discomfort glare, and in fact we know little about it. One hopes that some work will soon be commenced on this side of the problem.

§ 5. IMPORTANCE OF BRIGHTNESS AND CONTRASTS

That derivative of intensity, illumination, is slightly more useful as a conception than intensity itself, and also as a practical magnitude, but it is not by illumination that one sees. Illumination is a useful magnitude to the engineer or the architect who, like our tallow chandlers of old, chose to start the problem of seeing properly by providing sources of light. This has been certainly the easiest and most remunerative way to go about the business, but have its consequences always been favourable?

Suppose the craft of surgeons, represented in those days by the Worshipful Company of Barbers, had been powerful as well as enlightened physiologists. And suppose they had said: "This effort of the tallow chandlers to produce good seeing by providing candles is physiologically wrong and incidentally dangerous from the point of view of fire to our city. Man sees by contrast, and contrast alone, and contrast is produced by differences in brightness or in colour between an object and its background, or between the parts of an object. It is true you may sometimes have to assist matters by providing a little artificial light, but study to make your contrasts the best possible for seeing. Our clothing, our articles of furniture, the walls of our houses, the colour of our materials for surfacing pathways, all these factors which help to make things visible to the eye are being left to chance. They must in future be attended to. We will find out how the various contrasts make things visible, attract attention, and please the aesthetic sense, and study the colour and reflection factors of the paints and materials you use, and we will lay down standards. We will petition for a charter to give us the powers to enforce such standards." Is such an idea so far fetched as it may appear to some of us to-day? After all, it is not difficult to imagine a world in which artificial light-sources were non-existent and in which man had to manage to see by the light of nature, whatever that might be at the time, and by the artificial enhancement of contrasts. The lamp-maker as we know him to-day would of course not exist, and the world would be the poorer by the loss of a magnificent race of men. But would not their place be taken by an enormous industry supported by a century of painstaking research on the way in which we see—on paints, on colour combinations, and perhaps on luminescent materials?

There are of course examples of this sort of approach to be found in some special cases. Thus, where we want to make something particularly visible, such as a buoy at sea or a Belisha beacon or a survey pole on land, we so colour them as to produce arresting and hard contrasts with their backgrounds. Cricket screens and the white boards placed behind railway semaphore signals are other examples. And when we want something to be particularly invisible we copy the insects and birds, who knew all this long ago, and so colour it as to make its contrasts disappear and its outlines break up.

In any case a few centuries of postponement of the coming of artificial light sources, when the standards and magnitudes for appraising light could have been based on what one sees rather than on the operation of lighting, might have done wonderful things in keeping our sense of values right, and it might have produced a world of human surroundings much brighter and better than the one we know to-day.

There are not a few who to-day are restive under the tyranny of the candle and the foot-candle. Dr Luckiesh of the U.S.A. has tried in his writings to urge the engineer to appreciate the essentials of what he calls "the science of seeing". There is, for instance, the school of street lighting engineers and physicists who, because conditions for seeing are usually so difficult in street lighting, have had to study the essentials for good seeing under these exacting, though specialized, conditions. This has compelled them to ignore to a large extent the traditional fundamentals of illuminating engineering, and to seek a more rational basis for their appraisement of lighting.

I do not want to appear altogether to condemn the use of illumination as a gauge for lighting, provided it is not employed as a criterion for situations where it is of little use. For instance, Mr W. J. Jones has recently organized a most extensive and interesting survey of the illumination desired by ordinary people in the simple operation of reading a newspaper. Here illumination is clearly as effective a measure as brightness itself, because in such a test, with the black-on-white contrast of newsprint, the illumination is a sufficiently accurate gauge of the brightness. He obtains, for eyes adapted to a moderate brightness, a distribution curve for tests on 20,000 subjects, figure 10, showing that people on the whole prefer brightness produced by an illumination of 100 foot-candles on a surface which has a reflection coefficient of about 0·4. In other words, it has a brightness of 40 equivalent foot-candles. This value of brightness is in a sense surprisingly high, for the figure to which we are accustomed to in our homes or offices by artificial light is only of the order of 5 equivalent foot-candles, and in our offices by daylight from 20 to 100 foot-candles.

§6. MEASUREMENT OF BRIGHTNESS: INSTRUMENTAL

Where do we stand to-day in the technique of brightness measurement and in the expression of contrast for seeing? I am afraid we are not very far on when one remembers that colour contrasts as well as brightness contrasts enter into the problem.

The natural method of expressing brightness is of course in terms of intensity per unit area of the surface from which the light comes. Unless, however, the surface is very bright it is most inconvenient to measure directly intensity per unit area. Instrumentally it is more convenient to compare the brightness of the surface in question with that of another known surface illuminated to such an extent that the two surfaces match each other in brightness. The illumination of the known surface is thus a measure of the unknown brightness. In this way we eliminate the necessity of measuring areas, and can express the result in terms of foot-candles of illumination on a perfectly white surface. For simplicity rather than lucidity this latter unit of brightness has come to be termed the "equivalent foot-candle", or "foot-lambert". I am not proud of this term, but no one has found one which is more suitable and it is constantly employed for every-day work and translated into candles per square foot by dividing the equivalent foot-candles, as measured, by π.

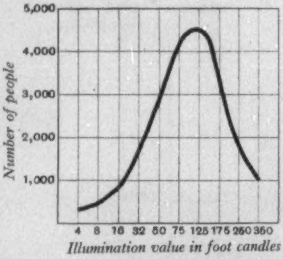


Figure 10. Frequency-distribution curve of values of illumination chosen by 21,179 persons for reading a daily newspaper.

My only reason for dwelling on this is that nearly all the measuring devices used for brightness are similar in principle to illumination photometers. In fact every visual photometer is a brightness photometer. When we wish to measure intensity, illumination or flux, we so arrange the instrument that a brightness is produced which is proportional to the quantity concerned. The surface whose brightness is to be measured is viewed in juxtaposition to a white surface of known adjustable brightness.

Photometers intended for measuring illumination by viewing the brightness of an illuminated test surface can also be used to measure other brightnesses, but in general, photometers intended for measuring brightness must be specially designed with very small external fields, for the vision of objects largely depends on brightnesses which subtend very small angles, and the detail of brightness distribution is very important.

Although it is true that the eye is a very bad photometer from the point of view of its absolute response, as a relative brightness photometer it beats most of our instruments in reliability and sensitiveness.

There are one or two simple rough and ready portable types of brightness meter, figure 11, whose accuracy may be put at ± 20 to 30 per cent.

Then there are optical brightness meters or telephotometers, figure 12, which are of two main types, the Maxwellian view type and the telescope type. In the Maxwellian type a lens system focuses an image of distant brightness on the pupil of the eye. The eye then sees the lens flashed with the brightness of the distant object and the lens becomes one of the two comparison surfaces of a photometer system. This type gives a large and conventional photometer field and measures the average brightness over a small angle. It is not, therefore, disturbed by any non-uniformity of object-brightness, but for small external fields it becomes unwieldy and costly, and there is difficulty in defining the object viewed. In the telescope type of brightness-measurer a small photometer field is inserted into the field of view of a telescope and its brightness is compared directly with that of the image of the distant object. The eye sees the telescope image with the photometer field superimposed. This type permits of the measurement of very small objects and the exploration of the detail. It is small and cheap and there is no doubt as to the object being viewed. It has the disadvantage of being difficult to use at low levels of brightness or with marked colour differences. A small telephotometer

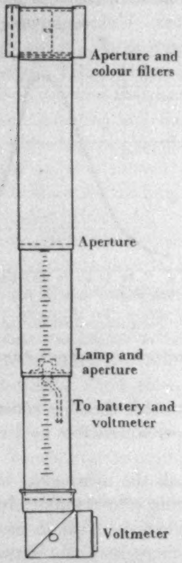
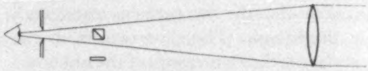
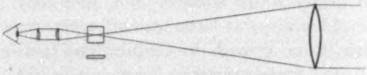


Figure 11. Diagrammatic arrangement of a brightness meter.



MAXWELLIAN TYPE.



TELESCOPE TYPE.

Figure 12. Diagrams of optical arrangements of telephotometers.

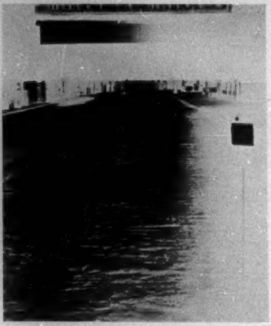


Figure 13. Photographic true-representation negative used in studying brightness under street conditions of lighting.

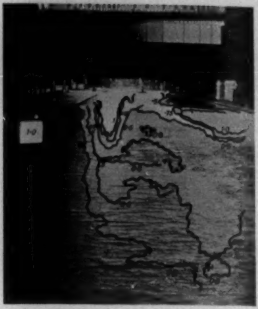
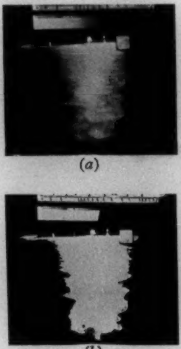


Figure 14. Positive of figure 13 with brightness contours added.



(a)

(b)

Figure 15. (a) contour of equal brightness obtained with contouring densitometer, (b) contour of equal brightness indicated by high-contrast photographic method.

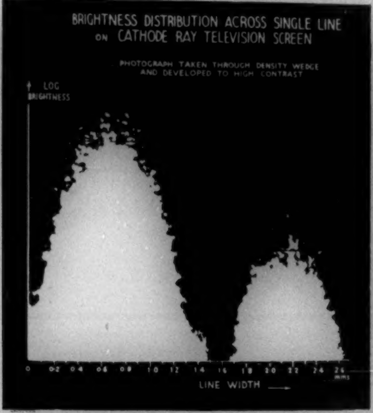
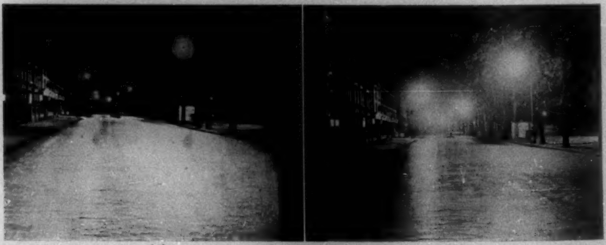


Figure 16. Brightness-distribution across single line on cathode-ray television screen at two different brightness-levels obtained by high-contrast photographic method.



(a)

(b)

Figure 17. Faithful (right) and flattering (left) representation of street lighting.

with a telescope multiplication of 10 can give a field as small as 3 minutes of arc. With a large telescope smaller fields could be used.

These photometers, if used for brightness survey, both involve some system of angular measure in addition to the photometer proper for determining the direction of view. Their accuracy under favourable conditions and when colour differences are not present may be of the order of ± 5 per cent.

§7. USE OF PHOTOGRAPHY IN BRIGHTNESS AND BRIGHTNESS CONTRAST MEASUREMENTS

Recently another way of appraising brightness has become more extensively used for many new problems. In this the photographic plate is used in an intermediate stage between the eye and the brightness to be measured. The photographic emulsion has some characteristics very much like those of the eye, both in kind and in degree. The eye has, among others, two sensitivities which we may call the photometric and the geometric; its sensitivity to the amount of light and its sensitivity to the direction of light. The first is a very variable and uncertain sensitivity and, as we have seen, we only use it as a test of equality, not in any absolute way. The second sensitivity, however, is very much more precise, and enables us to detect really extraordinarily fine detail in the objects we see.

The photographic plate is similar. It has a photometric sensitivity (by which it becomes blacker as it is exposed more) which is a rather variable quantity dependent upon many factors, and a geometric sensitivity or resolving power which is very much more precise. Once its vagaries are understood it can, by suitable technique, be used in a great variety of ways for the appraisal of light. Almost always it is used as an intermediary between the object to be appraised and the eye. The photographic plate can record not only the amount of light, but its position or direction; it can record a whole distribution at once, and it retains a permanent record for future photometry if necessary, and has several other unique advantages. For years, of course, it has been used in quantitative spectroscopy, and the way in which quantitative estimates of extremely minute amounts of material can be made through photography will be familiar to all physicists.

Generally, two methods of photographic photometry are possible. The first uses the amount of blackening of a plate to measure the light falling on it. If we use the plate to compare a series of unknown brightnesses with a series of known brightnesses, by comparing the densities of their images, fairly accurate results are possible. The method has, for example, been developed and extensively used for studying brightness under street lighting conditions, for which it is particularly suitable. Figure 13 shows such a photographic negative with its area of unknown brightness and with its known calibration brightness. We can plot out the brightness contours on a positive, figure 14, of the negative by means of the contouring densitometer. In this way the whole field of background brightness can be explored as well as, if necessary, that of objects seen against the background.

Sometimes the photographic emulsion is used in another way. There is a certain low exposure on the plate, below which nothing is recorded, and another high value above which no further increase of density occurs. If we use a very contrasty emulsion to take a photograph of non-uniform brightness, and print on to very contrasty paper, we can sometimes make the photograph show one contour of brightness without using any densitometer at all, figure 15. Here at (*a*) is one contour of a single bright area on a road surface from one light source. At (*b*) is a contrasty print from such an emulsion, showing how definitely and faithfully such a contour can be obtained. In figure 16 we have the distribution of brightness across the scanned line on the cathode-ray tube of a television receiver, at two difference brightness levels.

Another method of photographic photometry has been used by astronomers for years for determining the magnitude of stars. It depends on the fact that, owing to the nature of the light, imperfections in the object glass, unsteadiness of the air, and photographic spreading, the size of the image will vary with the brightness of the star according to the following empirical relationship

$$M = m - k/d,$$

where d is the diameter of the star image, m is the limiting magnitude of the photograph, k is a constant determined from known magnitudes on the plate, and M is the magnitude of the star as determined from the measured diameter d. The constants are determined from a sequence of known magnitudes determined by various methods, one of these being a coarse wire diffraction grating which when placed over the object glass produces images in the several orders, the ratio of the light in these being of calculable amount.

Still a further development, which is not a photometric method but is most useful in the appraisal of light, is the use of accurate photographic records—accurate in the sense that they convey, with sufficient precision for many purposes, the same impression to an observer as did the original scene. This again has been used as a technique for study of street lighting problems, and is a useful tool which can be used in parallel with the methods of photographic photometry to examine the characteristics of satisfactory and unsatisfactory distributions of brightness.

Here are two photographs* of the same street, figure 17. In one of them the artist has used all his craft to make the picture as flattering as possible. It gives us a picture which has little resemblance to the truth, and merely appears to be a temptation to the salesman of street-lighting fittings. In the other the tone values have been determined from a knowledge of the values of brightness existing in the street and of the properties of the eye, so that the photograph conveys, under the conditions in which it is viewed, the most accurate impression possible of the original installation(5, 6). Now that there is this quantitative way of securing correct tone values there would seem to be no excuse for many of the distorted photographs one is so often shown of lighting installations. In spite of its great advantages for some purposes, the photographic method makes great demands on the skill and patience of the experimenter; it is complicated, expensive, and comparatively inaccurate; nevertheless it has rendered possible many investigations which can be carried out in no other way.

---

* The lantern slides used to illustrate the lecture had regard to the properties of the projection lantern and the conditions of the theatre, the half tone illustrations in this paper are subject to limitations and do not faithfully reproduce the original prints.

§8. PHOTOELECTRIC BRIGHTNESS-MEASUREMENTS

Photoelectric brightness photometry is generally very difficult. The cell is essentially a device for measuring illumination, and has a comparatively large light-sensitive surface. In many brightness-measurements the angle of subtense of the object is very small, so that the flux available is excessively small, and consequently, both in order to collect sufficient flux and in order to keep the external field small, very large optical components would be required. For example, it has been possible touse this method for exploring the brightness distribution across a scanning line on cathode-ray tubes used in television, figure 18. In this case a fine slit is arranged to traverse a ten-times-enlarged image of the line, and a large-aperture short-focus (condenser) lens behind the slit condenses the light down on to the photocell cathode. This method is only made possible by means of the highly sensitive photoelectric photometer referred to earlier. Clearly this type of apparatus is too cumbersome for most types of brightness-measurement, but it is extremely useful for specialized applications.

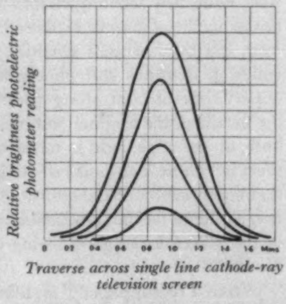


Figure 18. Distribution of brightness across single line on cathode-ray television screen, obtained with photoelectric brightness photometer.

§9. APPRAISEMENT OF CONTRASTS

I have already indicated that the chief aim in measuring brightnesses is to facilitate estimation of the contrasts by which we see objects. But there is the obvious objection in this that, whilst brightness contrasts may be measured, if there is a difference of colour the measurements have a very limited meaning. That is where our technique of measurement is so lamentably behind practical needs. Little has been done for directly appraising contrasts even when there is no colour difference. All we do is to measure the brightnesses of the two contrasted surfaces. And even when we have done so there is no accepted method of expressing them in terms of their ability to cause the eye to see them and the brain to appreciate them. I know we have the historic measurements of Fechner's fraction, which gives us the relative brightness difference which we just cannot see in terms of the background brightness. But these results do not help us to assess practical contrasts which are greater than the threshold. We know the percentage contrast which is just seeable, but seldom is it in threshold values that we are interested. The contrasts in the fields we look at are usually well above the threshold; they must be, if seeing is to be tolerable. An overcast day brings nearer to the threshold many contrasts which on a sunny day stand out clearly. But a fuller attention to the subject by the pioneers might have evolved in some cases sunlight contrasts with overcast skies. The architects of course have done much down the centuries to apply the principles of contrast to building facades. They had to, for they had no aids to lighting externally.

And when we come to colour contrasts our ideas are limited to certain qualitative impressions. We say that yellow is a good contrasting colour, and we probably have opinions on other colours or shades. But a technique is needed for appraising such contrasts other than on the threshold.

Recently the development of the television art has brought a new set of workers with some new techniques into the field of study of picture contrasts. This field has so far been mainly exploited by those interested in the photographic art. The work has been of high scientific merit, and the nomenclature chiefly in terms of emulsion densities and photographic results, but the television process gives an opportunity of controlling contrasts which has not hitherto been possible; for the details of the original picture as well as the details of the reproduced picture are both, at one stage, held in terms of electrical energy and can thus be manipulated—must in fact be manipulated—to give the most effective result. I cannot but believe that continuation of the effort, which television has started, to study the reproduction of scenes for the satisfaction of viewers will carry a stage further the appreciation of the principles of good seeing of pictures, of which the cinematograph industry has laid the foundation.

From a recent paper(7) on television images, it appears that the range of brightnesses in any picture used at present in television vary from about 15/1 to 120/1, while those used in cinemas vary from about 25/1 to 80/1. The television controls enable the contrast and brightness-range to be varied at will as the picture is viewed—a technique hitherto not easily achieved. It is possible to give an indication of the effect of changing contrasts by superposing two similar pictures, one very contrasty and the other very flat. The extent of the contribution of each picture to the combined picture is varied by means of a neutral absorbing wedge in front of each picture. Thus, within these limits, any degree of contrast is obtainable. Furthermore, any value of average field brightness is secured by increasing or decreasing the intensity on the projector lamps.

It is of particular interest to note the effect of changing contrasts when the average brightness of the picture is low. When the contrasts are made greater, although the maximum brightness is unchanged, we can note how much better is the seeing.

[A flat picture at a low value of brightness was shown on the screen, then the same picture with the same maximum brightness but with the contrasts increased.]

§ 10. APPRAISEMENT OF COLOURED LIGHT

In connexion with the use of gaseous and vapour light-sources for exterior lighting, there is a good deal of discussion and experiment directed to show whether or not it is easier to see in the yellow light of sodium lamps than in that of the less monochromatic sources. Dr Luckiesh has made a good effort to appraise sodium light under the categories of visual acuity, type-reading test, speed of seeing, and accentuation or otherwise of contrasts. He comes to the conclusion that on balance sodium has no practical advantage over other sources of light. Others contend, mainly on the basis of visual acuity, that it has an advantage, forgetting, I think, that the seeing of fine detail is not usually the chief desideratum in exterior lighting.

We can perceive how much we are at sea in appraising the practical value of the various coloured light sources by lighting some not unusual colours alternately with sodium light and with a light covering the whole spectrum. When this is done we can see now these contrasts, which are clearly marked under normal light, completely disappear or are reversed under sodium light.

By examining between 500 and 600 contrasts it has been found that contrasts which are already marked tend on the whole to be more so under sodium light, whilst those which are normally less well marked tend to be still less so with sodium light. I am calling attention in this way to the importance of colour contrasts with a view to showing how helpful it will be when principles for appraising them or techniques for studying them are better established.

There is such an immediate and pressing demand for simple techniques for measuring and specifying both the *colour* and the *colour rendering properties* of light sources, that we are likely to see a number of new proposals put forward in the near future.

In a desire to remain loyal to the internationally agreed trichromatic system, we should naturally turn to this system for a solution to our problems, but certain practical difficulties arise: Firstly whilst the *colour* of the light can readily be specified on the I.C.I. trichromatic system, the types of visual colorimeter obtainable on which such measurements can be made are unsuitable for making rapid routine determinations, as they require skilled observers to operate them.

A much simpler and more rapid technique for indicating the colour of a light source directly on the trichromatic system has recently been evolved;(8) this consists of three rectifier type photocells covered with suitable colour filters and connected respectively to three galvanometers. By an appropriate optical system the galvanometers project line images so arranged that, with the galvanometer at zero, these line images form an equilateral triangle. The light which is to be analysed for colour, falling uniformly on the three photocell components causes deflections of the three galvanometers and movement of the three lines towards the centre of the triangle. By adjusting the total amount of light falling on the cells there is one position where the three lines must intersect at one point, which therefore represents directly the location of the colour of the light source under test within the trichromatic system of the triangle.

Thus we have a ready means of measuring the *colour* but not the *colour rendering properties* of a light source. For we also want to know how the appearance of coloured articles and materials, etc., i.e. the colour of the reflected light, will vary with different illuminants.

Secondly the *colour rendering properties* of a light source will depend on its spectral energy distribution, which may be different for light sources of the same colour, that is having the same trichromatic coordinates. [The different colour-rendering properties of light from a high-pressure mercury lamp and from a tungsten filament lamp in front of which was a filter (daylight blue type glass) were then demonstrated.]

In what manner shall we specify the *colour rendering properties* of a light source? If we consider electric discharge lamps the spectral energy distribution is dependent not only on the nature of the discharge, but on the type and proportions of luminescent materials used to modify the colour of the light. Apart from attempting to modify the spectral distribution in a manner which will give an approximation to daylight, there are many cases where a 'warm' light is required. In these various cases we have to devise methods of appraising the colour-rendering properties of the source.

Already many methods have been suggested, either based on measurements of relative energy or luminosity in various spectral bands, or on the visual judgement of the apparent colour of coloured materials, etc., when viewed under the various light sources. These methods have their uses, but are rather laborious, and liable to give misleading results.

Having, in the photoelectric colorimeter referred to earlier, a very quick method of measuring colour, why should we not make use of this to measure the colour-rendering properties? For example, if we determine the colour of the light source, and also the *colour* of the light reflected from, or transmitted through, a suitably selected group of coloured materials, or filters, the relative position of these points in the colour triangle should enable not only the colour but the colour-rendering properties resulting from the particular form of spectral distribution of the source to be determined. It will be obvious that in this case two sources which appear the same colour but are different in spectral distribution should be differentiated by the different values of the trichromatic coordinates of the reflected or transmitted light, from or through the coloured media.

The attraction of this method is that we use only the internationally agreed trichromatic system, and can make our determinations at routine photometric speeds on one type of apparatus. Also, perhaps equally important, such results are closely related to what we see when looking at coloured articles or materials under different types of illuminant.

Meanwhile we are finding many practical cases where the new line spectra light sources are, on account apparently of their colour, giving better seeing in various industrial operations. For instance, the new mercury light is being used to advantage in collieries on the picking belts to aid the distinction between coal and shale, also in the Rand on ore sorting belts where the presence of gold in ore can be better detected.

In galvanizing, the detection of flaws is made easier and in laundry work, scorches and iron mould show up more readily. In the pottery industry cracks and blow holes are more easily detected in the early stages of firing—and this light has also proved more effective when inspecting for flaws in glass or for dirt in washed milk bottles.

The explanation of the real cause underlying the improved seeing in each of these cases might be instructive and may possibly be different for each one. I merely mention them to show that the subject is not an academic one.

Sodium lamps on account presumably of their monochromatic character are of course of use where very fine detail has to be detected.

§ 11. INTRINSIC BRIGHTNESS OF LIGHT SOURCES

Under proper conditions of utilization of light for general lighting purposes it does not usually matter how bright the source of light itself is, for the art of diffusing light is well understood although perhaps not always practised. Therefore for general lighting we are more concerned with the brightness of the glassware used in diffusing the light, than with the brightness of the source of light itself.

Source of light	Approximate intrinsic brightness (can./cm^2)
Carbon filament	20
Tungsten filament (gas-filled lamps)	350 to 1,650
Sodium lamps	c. 10
High-pressure mercury 1 atmosphere, 230 v.	160
High-pressure mercury 125 w. pearl bulb	50
Brightness of column alone	1,000
Mercury water-cooled, 400 w./cm., 300 v./cm. *	30,000
Mercury water-cooled, 800 w./cm., 400 v./cm.	60,000
Ordinary carbon arc	13,000 to 17,000
High-current-density carbon arc	50,000 to 80,000

* Starting volts double running volts.

But when used for projection purposes the intrinsic brilliance of the source becomes vital; and it is not always realized how brilliant some of the new sources of light are, over what wide limits their brightness ranges, and what potentialities these have for projection.

Four or five years ago, you will remember, it was found that very great yields of light could be obtained by the passage of electricity through mercury vapour if the pressure of the vapour was increased. Some of the lamps which have resulted from this are well known now. Others are more experimental.

[Enlarged images of three different types of mercury vapour lamps were thrown on the screen, one a well known lamp widely used for street lighting had a brilliancy of about 160 candles per sq. cm. compared with about 1000 candles per sq. cm. of a tungsten lamp filament. The second lamp was smaller with a high vapour pressure, and had a brightness of about 1000 candles per cm^2, i.e. some six times brighter. Another lamp had at the top a water cooled envelope to dissipate the heat from the area round its very small and brilliant discharge column. The brightness was of the order of 30,000 candles per cm^2 or thirty times brighter than the last.]

The increasing brightness obtained with such lamps begins to make them comparable in brilliancy with high current density arcs used for searchlights and cinema projection. We can press our ionized columns further still, the only limit being our ability to carry away the heat. If we do this the quartz lasts only a few minutes or seconds even when cooled with water. [The lecturer then showed a lamp with a brilliancy approaching 150,000 candles per cm^2 a brilliancy comparable with that of the sun.]

The eye is an extraordinarily bad judge of brilliancy. We usually under-estimate enormously a difference which may exist between the brightness of two sources, unless they differ in total candle power, when the brighter source may sometimes be mistaken for the less bright. The table of brightnesses of typical sources will indicate the range which is within prospect. Some of the higher brilliancy sources in this table have not as yet gone beyond the laboratory stage.

This review of some of the techniques in use in the study of lighting and seeing has, I know, been disjointed and incomplete. In the compass of a short lecture this is inevitable. I tried to choose those aspects of the subject which seem to me to give the clearest picture of the art as it is to-day. If anyone troubles to criticize me I know I am vulnerable in my omissions. But I would ask such critics to bear in mind that I set out to demonstrate the state of an art mainly through the techniques which are in use for its study. As these techniques have become available during the past thirty years the art has changed and advanced greatly. Like so many other subjects, however, that of lighting and seeing has been and is held in check by the inevitable tendency of those who practise it to define it at any epoch in terms of the quantities which they can measure and the techniques they can understand. The illuminating engineer of yesterday was the candle power engineer of the day before. He is becoming the brightness engineer of to-day, but as soon as physics has provided suitable and understandable techniques for appraising contrasts he is surely fated to-morrow to become a contrast engineer. Whereas research can stretch out where it pleases, it is difficult for a practical art to advance faster than the established techniques for appraising its merits.

REFERENCES

(1) *G.E.C.Jl.* **5**, 125 (1934).
(2) *G.E.C.Jl.* **6**, 205 (1935).
(3) Stiles, W. S. *D.S.I.R. Tech. Pap. Illumin. Res., Lond.*, No. 8.
(4) Stiles, W. S. and Crawford, B. H. *Proc. roy. Soc.* B, **116**, 55–102 (1934).
(5) Hopkinson, R. G. *Trans. Illum. Engng Soc., Lond.*, **1**, 19 (1936).
(6) Hopkinson, R. G. *Photogr. J.* **76**, 323–48 (1936).
(7) Jesty, L. C. and Winch, G. T. *Trans. Illum. Engng Soc., Lond.*, **2**, 104 (1937).
(8) Winch, G. T. and Palmer, E. H. *Trans. Illum. Engng Soc., Lond.*, **2**, 137 (1937).

DEMONSTRATIONS

STRUCTURES PROPOSED FOR PROTEIN MOLECULES

Demonstration given on 12 *November* 1937 *by* D. M. WRINCH, M.A., D.Sc., Oxon., D.Sc., Lond., *The Mathematical Institute, Oxford*

Proteins constitute a large class of chemical substances which take part in a wide variety of biological reactions. The work of Svedberg and his collaborators(1) has shown that there exists a number of proteins which possess a certain molecular status, in that in solutions of appropriate *p*H they consist of globular molecules of definite molecular weight. These molecular weights, it is found, are not distributed at random, but fall into a sequence of widely separated classes. Work on protein films further shows that certain globular proteins in solution spontaneously form monolayers, which have characteristic mechanical properties(2).

[Built up protein films by Langmuir and Wrinch and by Wrinch and Marler are shown.]

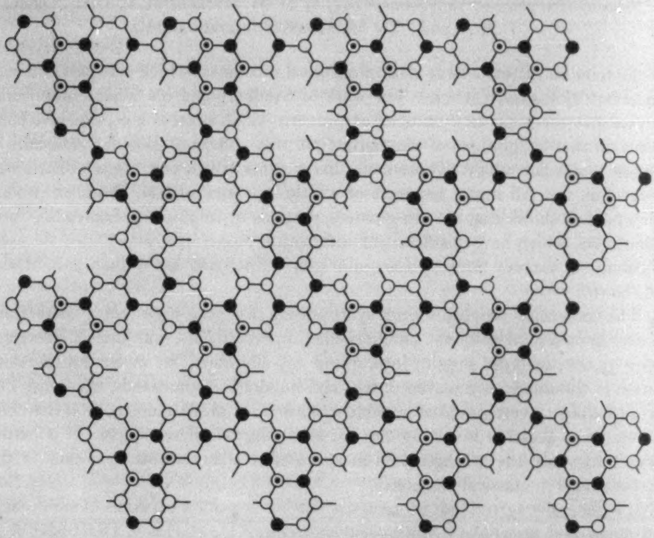
The molecular weights found by Svedberg are very high; they range from 18,000 up to several millions. One specially important class, with molecular weight about 35,000, includes pepsin, insulin and egg albumin. The molecules therefore consist of thousands, some even of tens and hundreds of thousands, of atoms. The comprehensive investigation of possible structures for protein molecules is therefore necessarily a question involving the use of mathematical technique. It is hardly feasible to study the arrangements in space of so many atoms by means of the methods used in classical chemistry.

It is generally agreed that proteins are polycondensation products of amino-acid and imino-acid molecules. Amino-acid molecules $\mathrm{NH_2}$—CHR—COOH have in all cases a common skeleton N—C—C. About 25 or 30 different varieties have so far been found among the degradation products of proteins, each characterized by a special *R*. *R* may be purely aliphatic, it may have an aromatic constituent, or it may contain basic or acidic groups. It is a remarkable fact that all these units, whatever *R* may be, prove to have one uniform configuration as regards the C atom carrying the *R* group(3). It is further generally agreed that unit is joined to unit in these polycondensation products by the formation of a link between the N atom of one and the terminal C atom of the other. The problem of the structure of proteins therefore requires the consideration of all possible arrangements in space of the building units, unit being linked to unit by ...N)—(C... bonds. In the cyclol theory of protein structure(4) an attempt has been made to devise structures fulfilling the given conditions. It is to be regarded simply as a first step towards a comprehensive investigation of the problem which will require the application of group theory and of the theory of partitions and the development of new types of geometry of position.

The amino-acid residue, the building unit for proteins, can be written in two ways:

$$-\mathrm{HN}-\mathrm{CH}R-\mathrm{CO}-; \quad >\mathrm{N}-\mathrm{CH}R-\mathrm{C(OH)}<$$

In the first case only one-dimensional polymers are geometrically possible; these can be open or closed. In the second, two-dimensional or even three-dimensional polymers are geometrically possible. The full geometrical investigation of possible structures for protein molecules which satisfy the given conditions necessarily requires the discussion of all these polymeric types. In the polypeptide theory of protein structure only open one-dimensional polymers were contemplated. One-dimensional polymers consisting of as many as 18 units in open chains were subsequently built in the laboratory. These substances proved not to be proteins. Closed one-dimensional polymers, with the exception of diketopiperazine molecules consisting of two units, were not contemplated and have not yet been built in the laboratory. Attention is therefore directed to possible structures consisting of closed one-dimensional polymers and also to two-dimensional or even three-dimensional polymers.



(Reproduced by permission of the Royal Society)

Figure 1. The cyclol pattern. The median plane of the lamina is the plane of the paper. The lamina has its "front" surface above and its "back" surface below the paper. ● =N; ○ =C(OH), hydroxyl upwards; ⊙ =C(OH), hydroxyl downwards; ○— =CHR, direction of side chain initially outwards; ○- =CHR, direction of side chain initially upwards.

One special class of two-dimensional polymers, the cyclol fabric, has been investigated in some detail. This two-dimensional atomic network or fabric is shown in figure 1. The uniformity of all the amino acids already referred to implies that such a fabric is dorsiventral; all *R* groups initially emerge from its front surface and none from its back surface. These experimental facts thus find a fundamental interpretation on this theory, suggesting in fact that the essential entity in proteins is a dorsiventral fabric. The findings regarding the existence and nature of protein films thus fall into place in the general scheme. Furthermore, an investigation of the geometrical nature of the cyclol fabric discovers that such a fabric can be folded round so as to lie on the surface on certain polyhedra and form closed, cage-like structures⁽⁵⁾. These it is suggested are the globular proteins which in solution form monolayers simply by the ripping open of these closed cage-like structures. On this view protein monolayers are simply geometrical isomers of globular proteins, and consist of polymers or associations of pieces of the cyclol fabric.

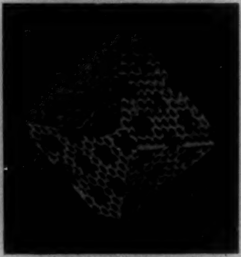


Figure 2. The C_2 structure. [Photograph taken by F. M. Beltjens, Leyden]

The metrical requirements of the constituent atoms show that only certain polyhedra are acceptable, and further that such polyhedral cyclol structures exist in series which consist of specific numbers of units given by quadratic functions of the natural numbers. These deductions explain the results of Svedberg in general terms, each molecular weight class on this interpretation connoting one closed cyclol or an association of a certain number of such cyclols.

At present it has proved possible to construct only one series of closed cyclols $C_1, C_2, \ldots, C_n, \ldots$. The polyhedral framework in each case is a truncated tetrahedron and the number of units in C_n is $72n^2$. Models of C_1, C_2, C_3 and C_6 are shown. (See also the photograph of C_2 in figure 2.) The C_2 structure containing 288 units is of special interest. Its molecular weight apart from attached water molecules is, say, 36,000, assuming a mean residue weight of 125. The suggestion was therefore made in 1936 that this may be an appropriate structure for insulin, pepsin, egg albumin and the other globular proteins which have molecular weights in the neighbourhood of 35,000⁽⁵⁾. It has since been stated by Bergmann and Niemann⁽⁶⁾ that the chemical analysis of egg albumin allows the deduction that each molecule of this substance contains 288 amino-acid residues. It has further been found that the C_2 structure fits adequately with the measurements found from the X-ray analysis of the lattices of pepsin⁽⁷⁾ and insulin⁽⁸⁾. It is hoped to subject the predictions of the theory to further and more detailed test by the application of physical techniques, including the use of electron-diffraction.

REFERENCES

(1) Svedberg. *J. Amer. chem. Soc.* (1929 *et seq.*).
(2) Gorter. *J. gen. Physiol.* **18**, 421 (1935), etc.
Schulman and Rideal. *Biochem. J.* **27**, 1581 (1933), etc.
Langmuir, Schaefer and Wrinch. *Science*, **85**, 76 (1937).
(3) Jordan Lloyd. *Biol. Rev.* **7**, 256 (1937).
(4) Wrinch. *Nature, Lond.*, **137**, 411, **138**, 241, 651 (1936); **139**, 718 (1937); *Proc. roy. Soc.* A, **160**, 59 (1937).
(5) Wrinch. *Nature, Lond.*, **139**, 972 (1937); *Proc. roy. Soc.* A, **161**, 505 (1937).
(6) Bergmann and Niemann. *J. Biol. Chem.* **118**, 301 (1937).
(7) Wrinch. *Phil. Mag.* (in the Press).
(8) Wrinch. *Science*, **85**, 566 (1937); *Trans. Faraday Soc.* **33**, 1368 (1937).

Magneto-damping in nickel

Demonstration given on 26 *November* 1937 *by* Mary D. Waller, B.Sc., F.Inst.P.

The subject of this demonstration was the outcome of some acoustic studies made on metals and special alloy steels⁽¹,²⁾ in order to determine how the internal damping is affected by various physical conditions.

A pure hard nickel rod, kindly supplied by Messrs Henry Wiggin and Co., Ltd., was suspended horizontally at the two nodes (0·224 of the length from either end) by means of two fine threads, and struck with a hammer. The note emitted remained audible for some seconds. This procedure was repeated after the specimen had been placed in a magnetizing field of about 100 gauss, when it was found that the note died out three or four times more rapidly. For purposes of demonstration in a large room, a rod about 12 cm. long and about 1 cm. in diameter, which vibrated at 2570 c./sec., was readily audible, but the phenomenon was also demonstrated with a thinner and with a thicker rod.

A typical set of observations, made with the ear in a standard position and using a stop watch is shown in figure 1, in which the abscissa shows the strength of the magnetic field to which the specimen was subjected, while the ordinate shows the subsequent duration of audibility in seconds. The magnetic condition of the rod in figure 1 can be inferred from the hysteresis curve given in figure 2. Points to be noted in connexion with figure 1 are the horizontal part of the curve at *A* for weak fields, the steep part of the curve (corresponding to the steep part of the *AB* hysteresis curve), the impossibility of restoring the vibrating properties except by thoroughly demagnetizing the specimen, and the two maxima at fields which are near to, but exceed the coercivity.

Similar observations have been made with a more highly damped annealed pure nickel rod, and with rods made of commercial nickel, iron, cobalt (kindly given by the Brandhurst Co., Ltd.) and a number of Sir Robert Hadfield's special alloy

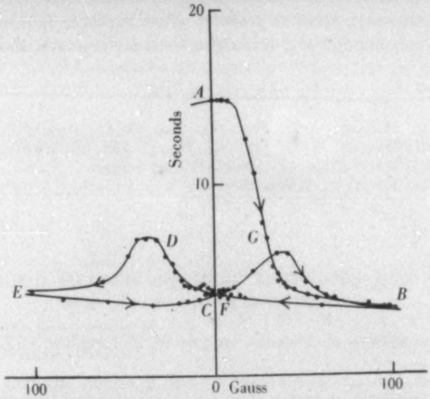


Figure 1. Variation of duration of audibility of vibrating nickel bar with intensity of magnetic field previously used to magnetize it.

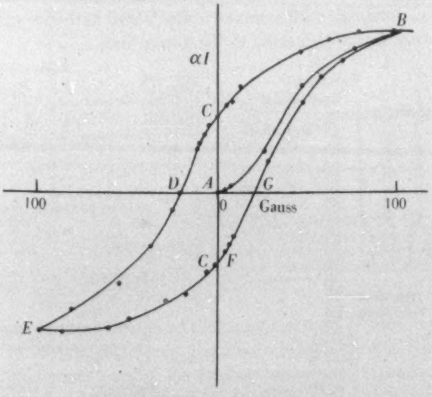


Figure 2. Hysteresis curve.

steels⁽²⁾. The effect is greatest with nickel and greater with cobalt than with iron. Kerston⁽³⁾ has explained the increase of damping which occurs in the magnetized condition as being due to eddy currents occurring in the oscillating body; I have found that the effect is too small to be detected in some of the magnetic alloys investigated. The increase in damping in the case of nickel is comparable with that which can be produced by suitable mechanical and heat treatment.

Since vibration damping is of considerable importance in engineering practice(4), and since it is a structure-sensitive property which depends upon so many physical conditions, a simple method of observing it, such as the above, should be of value.

REFERENCES

(1) Waller, M. D. *Proc. phys. Soc.* **46**, 124 (1934).
(2) Waller, M. D. *Proc. roy. Soc.* A, **156**, 383 (1936).
(3) Kerston, M. *Z. Metallk.* **27**, 97 (1935).
(4) Föppl, O. *J. Iron Steel Inst.* p. 393 (1936).

A PLANE-ELECTRODE DEMOUNTABLE THERMIONIC TUBE USED AS A GENERATOR OF ULTRA-HIGH-FREQUENCY OSCILLATIONS

Demonstration given on 26 *November* 1937 *by* W. A. Leyshon, Ph.D., F.Inst.P.

The apparatus demonstrated was set up with the main object of obtaining more information in regard to the generation of ultra-high-frequency oscillations by a method previously described to the Society(1). In this method an experimental tube was used in which the electrode system consisted of two parallel plane grids at the same positive d.c. potential, with symmetrically placed kathodes external to them. A Lecher-wire system was connected to the two grids.

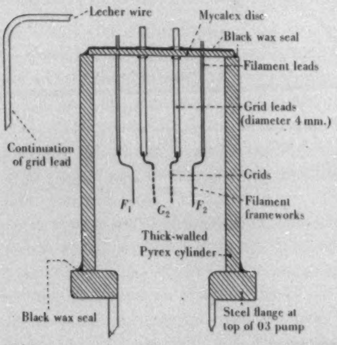

Lecher wire
Mycalex disc
Black wax seal
Filament leads
Grid leads (diameter 4 mm.)
Continuation of grid lead
Grids
Filament frameworks
F_1
G_2
F_2
Thick-walled Pyrex cylinder
Black wax seal
Steel flange at top of 03 pump

Figure 1.

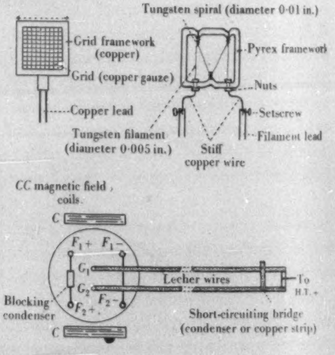

Tungsten spiral (diameter 0·01 in.)
Grid framework (copper)
Grid (copper gauze)
Pyrex framework
Nuts
Copper lead
Setscrew
Tungsten filament (diameter 0·005 in.)
Stiff copper wire
Filament lead
CC magnetic field coils
C
F_1+ F_1-
G_1
G_2
F_2-
F_2+
Lecher wires
To H.T.+
Blocking condenser
Short-circuiting bridge (condenser or copper strip)
C

Figure 2.

In the present apparatus simplicity of design and working was aimed at; it may in fact be termed transportable—it has on two separate occasions been transferred to Oxford, without air being let into the tube. The tube is continuously evacuated by a pumping system consisting of two Metropolitan-Vickers oil condensation pumps (02 and 03 in series) backed by a Hyvac pump. The construction of the tube is shown in figures 1 and 2. Tungsten wires of diameter 0·005 in. were finally, after a considerable amount of preliminary experimentation, chosen for the filaments. Sufficient emission is obtained with filament currents of the order of 2 amp. Mycalex is used as the material for the lid of the valve because of its low loss at high frequencies. All the demountable joints are sealed with Apiezon black wax.

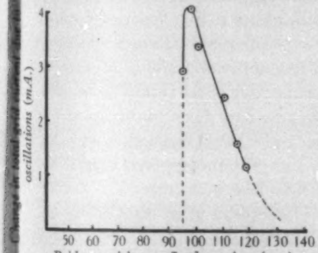


Figure 3. Typical graph showing relation between length of Lecher wires and change in grid current. *Valve* 8: $v_{g1}=v_{g2}=186$ v.; $i_{g1}+i_{g2}=25{\cdot}5$ mA.

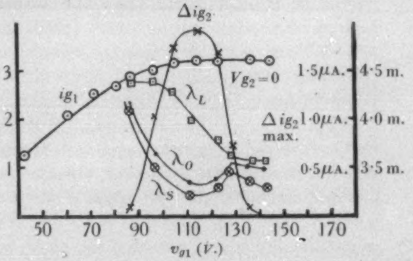


Figure 4. *Valve* 5: One (F_1) filament emitting; outer grid G_2 at zero potential; i_{g1}, current to inner grid G_1; Δi_{g2}, change in current to outer grid G_2 due to oscillation; λ_L, λ_O, λ_S, longest, optimum and shortest wave-length generated.

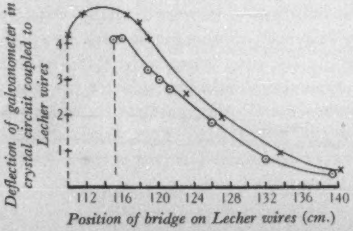


Figure 5. Showing effect which may be produced by the application of a longitudinal magnetic field. *Valve* 10: $v_{g1}=v_{g2}=70$ v., $i_{g1}+i_{g2}=4{\cdot}85$ mA.; ⊙ without magnetic field; × with magnetic field (*ca.* 12 gauss).

The Lecher wires are copper tubes of the same diameter as those used as electrode leads inside the valve, and they are at the same distance apart as these leads. Thus, as will be seen from figures 1 and 2, the Lecher-wire system is practically continuous up to the electrodes (grids) themselves.

Degasing, which in the first instance took some considerable time, is assisted by internal heating due to the hot filaments and, when the vacuum is sufficiently high, by bombardment with electrons and positive ions. At a later stage of evacuation this process is further accelerated by the generation of high-frequency oscillations. The degree of vacuum is estimated by the backlash ratio, i.e. the ratio of (positive) outer grid current to (negative) inner grid current, the inner grid (i.e. that nearer the emitting filament) being held at a potential of 160 V. and the outer at -4 V. relative to the negative end of the filament. It is found that oscillations will, in general, start when this ratio is of the order 5×10^{-5}. The limiting ratio attainable with no special arrangement for cooling the wax seals, or for shielding them from bombardment by stray electrons, is about $2{\cdot}5 \times 10^{-5}$. For the electrical circuit use is made of the 220 V. d.c. mains to provide both filament current and high tension, or part of the latter. It will be noted, figure 2, that the negative ends of the filament leads are connected directly, and the positive ends through a blocking condenser. The possibility of large ultra-high-frequency variations of kathode potential due to standing waves on the filament connecting wires is thus minimized.

With this apparatus a large number of observations have been made in order to find out how the generated wave-length depends on the length of the Lecher wires, the distance between the electrodes, transparency of the grid, the applied voltages, the kathode emission, and the applied magnetic field. The investigation is not yet complete, nor is the apparatus in its final form. However, a great many of the observations previously recorded for plane or cylindrical valves have already been repeated with it. Some typical results are shown in figures 3 to 5.

The tube can be made to act as its own degasing agent, by heating, bombardment, and generation of ultra-high-frequency oscillations; it can be made to give an indication of the degree of vacuum reached within it; the attached Lecher-wire system can be used for the measurement of the wave-length of the oscillations generated, and to give information in regard to the effective impedance of the electrode system at the frequency of these oscillations. In a perfected form (in which it is possible to adjust the distances between the kathodes without the tube having to be demounted) the apparatus should be useful for teaching purposes.

The kathode frameworks and other parts of the valve structure were made in the Electrical Laboratory at Oxford, where Prof. Townsend has most kindly allowed me to work during summer vacations. The cost of the research has been covered by grants from the Waller Research Fund.

REFERENCE

(1) Leyshon, W. A. *Proc. phys. Soc.* **48**, 489 (1396).

REVIEWS OF BOOKS

An Outline of Atomic Physics, by Members of the Physics Staff of the University of Pittsburgh. Pp. ix + 414. (John Wiley and Sons Inc. New York. Chapman and Hall Ltd. London. Second Edition. 1937.) 18*s*. 6*d*. net.

The book grew out of a course of lectures designed for college students who, having completed a year's work in physics, were proceeding to qualify themselves for some other profession. It was hoped, by taking them to the frontiers of physics and giving them some intelligent appreciation of what was going on there, to awaken in them a love of it and a respect for its achievements; feelings which a first-year course in physics too often leaves unstimulated. The book covers the range of subjects to be expected from its title, and in addition there are chapters on the kinetic theory of matter and on astrophysics.

The book admirably fulfils the purpose for which it was designed. While avoiding the mass of detail and the formal mathematical development which are essential in a textbook for specialist students of physics, the authors are not afraid of making calls on the intelligence of the reader, and for the most part succeed in conveying the physical argument in a clear and intelligible form. The book is illustrated with photographs and numerous diagrams. For the second edition it has been thoroughly revised in the light of recent discoveries, and a new chapter on nuclear structure has been added. J. A. C.

Hydro- and Aerodynamics, by S. L. GREEN. Pp. viii + 126. (London: Sir Isaac Pitman and Sons, Ltd.) 12*s*. 6*d*.

Where *does* the student of physics, or of mathematics, acquire his introduction to the theory of the motion of fluids? Clearly, if he is to carry the matter far, he will have to read Lamb at some stage (and do let us disabuse our students of the idea that it is difficult, or that it involves very advanced mathematics), but with what shall he precede this? The textbooks of theoretical physics generally contain a chapter or two on the subject, but since Besant and Ramsey fell into disuse there has been no good introduction, as far as the present reviewer is aware.

Without question, this book fills the gap for the student of mathematics. It contains the necessary minimum to enable it to serve as a starting point, whatever road the student is intending to travel later: the equations of motion of the inviscid fluid, irrotational motion and the application of conformal transformations both to continuous and to jet-like flow, vortex motion and wave motion, with a final pair of chapters on viscous fluids and on flow at high Reynolds numbers. In these last two chapters the treatment is fragmentary and would for most readers require supplementing by a more physical treatment such, for example, as is found in treatises on general physics. Although the subtitle states that the book is for advanced students of aeronautics, hydraulics, physics and mathematics, there is little discussion of gases (the flow of a viscous fluid through a tube is only carried out for the incompressible case) and no discussion of the resistance of bodies at moderate and high Reynolds numbers. It is not suggested that this last could be treated in any detail, since mathematical advances are only now proceeding in a halting manner; but an indication of the nature of the results, and an explanation of the utility of dimensional theory, would have added to the value of a book which is already extremely good.

J. H. A.

Sound, by A. T. Jones. Pp. xii + 450. (Chapman and Hall). 20*s*.

Dr Kaye in his Presidential Address before Section A of the British Association said that "acoustics, far from being a Cinderella, has become a radiant Princess of physics in whose career the public interest has become completely enchained". One illustration of this fact is the increasing number of textbooks on academic and applied acoustics which are now appearing, a symptom of the interest which universities are taking in this subject. The textbook which Prof. A. T. Jones has written is remarkable for the amount of advanced acoustics it covers without the use of complicated mathematics. In fact, it almost entirely avoids mathematics. (An indication of the type of reader for which it caters can be obtained from the footnote on p. 28: "If the reader has forgotten what a logarithm is, he may refer to Appendix 4"). This does not mean that the mathematics is replaced by tedious argument —far from it. The explanations are almost invariably brief and interesting. A remarkable feature of the book is the sets of problems which appear at the ends of the sections. These are not set to test book knowledge, but always to extend the reader's learning by making him think beyond what has been discussed. Sometimes they do more than this, even; for example: "What is the objection to explaining thunder by the bumping of clouds together?" Another question is rather longer; "A story was once written about an Arctic expedition on which the men encountered a bitterly severe cold spell. The cold was so intense that the men had difficulty in understanding each other and finally were unable to hear at all. Their words were frozen before there was time for them to be heard. When the cold became less intense the frozen speech began to thaw out and words and sentences spoken days or weeks earlier were heard at last. We smile at this story, but what is the matter with it?" It is just possible that questions of this type will render a lecturer's life a little more arduous. Another form of this question appears in connexion with electrically maintained tuning forks. After devoting a paragraph to putting forward an explanation of the action of a maintained tuning fork, he puts the question: "What is the fallacy in the above argument?"

The book contains the usual chapters on vibrating motion, combination of tones, musical scales, sound transmission, free and forced vibrations, speech and hearing, musical instruments and technical applications. Of these one might single out the chapters on speech and hearing, musical instruments, and technical applications as being especially good. There are one or two misprints and one or two comparatively unimportant errors. Doubtless these will be put right in the next edition.

The book may be recommended to physics students, musicians and the general public alike.

J. E. R. C.

A Text-book of Light, by G. R. Noakes, M.A. Pp. x + 355. (London: Macmillan, 1937.) 6*s*.

This book is intended for students working to the syllabuses for the higher school certificate, university scholarships, first M.B., etc. It incorporates many of the recommendations in the Physical Society's *Report on the Teaching of Geometrical Optics* (1934), including one of the two alternative sign conventions in which focal length and dioptric power take the same sign, instead of opposite signs as in the Cartesian system used in the older textbooks. The convention chosen by the author is the non-Cartesian one in which all real distances are positive and all virtual distances negative; the reasons for the choice are that pupils consider it to be less artificial than the older Cartesian system and that the average worker makes fewer slips. It is for these very reasons, however, that many teachers prefer the other alternative recommended in the *Report*, namely the Cartesian system in which the initial direction of the light is taken as positive. The calculus is used, and photometry, optical instruments, polarization, ultra-violet radiation and X rays are dealt with at some length. In the reviewer's opinion, photometry is dealt with much too early, as in many elementary books on geometrical optics. The text is illustrated with 276 figures, which, with few exceptions, are carefully drawn. Notable exceptions are figures 20 (Lummer-Brodhun photometer), 104 (Pulfrich refractometer), 107 (erecting right-angled isosceles prism) and 208 (prism spectrometer), all of which might well be improved in a future edition. Examination questions are given at the ends of chapters, and the answers at the end of the book.

W. J.

Fundamentals of Physical Optics, by FRANCIS A. JENKINS and HARVEY E. WHITE. Pp. xiv+453. (New York and London: McGraw Hill, 1937.) 30*s*. net.

Starting where the simple principles of geometrical optics leave off, the authors have devoted the whole of this book to the so-called classical physical optics or wave optics, to the exclusion of any systematic discussion of the quantum theory and its application to spectra and atomic structure. The reason for this is twofold: consideration of space, and the recognition of the complementary wave and quantum aspects of light as equally important, but quite distinct, fields of knowledge. In covering only the first field, the book has achieved a unity which would have been lost by the inclusion of a necessarily brief treatment of the second. Nevertheless, in the later chapters dealing with the interactions of light and matter, the authors have been careful to point out the limitations of the classical wave theory and the necessity of the quantum theory for a complete explanation of observed phenomena. The choice of subject-matter and method of development are the result of many years of teaching by Prof. R. T. Birge, the authors, and others in the department of physics in the University of California, Berkeley. In the development of the subjects of interference, diffraction, dispersion polarization, etc., emphasis is placed on the physical explanation of the phenomena, and graphical or vector methods are freely used to supplement the mathematical treatment. In addition there are chapters on fluorescence and phosphorescence, light-sources, dielectric and metallic reflexion, electromagnetic theory and magneto-optics and electro-optics. The text is illustrated throughout with diagrams and photographs, most of which are by the authors themselves. It is in classical physical optics that perhaps the most beautiful and striking experimental demonstrations in physics are to be made. Descriptions of many of these are given throughout the book, divided from the main text by horizontal lines. Another pleasing feature is the inclusion of brief biographical footnotes. Each chapter ends with a number of problems. The book is well indexed, excellently produced, and can be unreservedly recommended to honours students.

W. J.

Trigonometry: Part II, Higher Trigonometry, by T. M. MACROBERT and W. ARTHUR. Pp. xiii+137. (London: Methuen and Co.)

Starting as the study of triangles, an adjunct of geometry (the measurement of land), trigonometry soon finds the advantages of introducing the sine, cosine and tangent. We may, for the purposes of classification, say that elementary trigonometry considers these in their geometrical aspects, but when they are studied for their own intrinsic interest we soon find that they are intimately related to the exponential function, and therefore of course to its inverse, the logarithmic function. Consequently they are appropriately studied in courses of analysis, or in the theory of functions, and the methods of these sciences are helpful. In previous generations it was the custom, either in the spirit of mortifying the flesh or else from a Houdini-like joy in overcoming obstacles, to write books on higher trigonometry in which the results obtained elsewhere by the methods of the calculus were deduced by pure algebra. This rather pointless procedure has now been dropped, and in the book under review the most convenient method available is used in each case. It is not intended for advanced students, and therefore opens with chapters on complex numbers and, after proving de Moivre's theorem, proceeds to the familiar applications in various fields. It then takes up the notion of a limit, deals with those various finite and infinite trigonometrical series which most of us can never remember without a book of reference, and concludes with a good treatment of the logarithmic function. On the way various useful sidepaths are explored, such as the evaluation of certain types of definite integral. The book is certainly one to recommend, and not least among its virtues are the very numerous, well-chosen exercises.

J. H. A.

Science and Music, by Sir JAMES JEANS. (Cambridge University Press.)

This book is a welcome addition to those which seek to explain to the musician the working of his tools, and it is sincerely to be hoped that he will take advantage of it. Musicians are notoriously supercilious about acoustics, pointing out that their art was old when the science of acoustics was still young, and that—as the physicist would be the first to admit—the science has still some leeway to make up before it is abreast of the empirical discoveries of the musical instrument makers. The reputation of Sir James Jeans as scientist and author is such that musicians can scarcely ignore the experimental science of recent years, where it touches music. In particular, we hope that the author's exposure of the psychological self-delusion involved in the appraisement of "pianoforte touch", "key character", etc., will sink in. No one could write a book of this nature without drawing on the resources of his predecessors, and Sir James Jeans is quite frank in this matter. It was his intention, he tells us, to bring Helmholtz up to date, but the book as it stands is better than that; it deals with all the aspects of playing and listening to music on which physics has anything to say. Indeed, the section which is mostly Helmholtz, that on musical scale, is perhaps the least inspiring part of the book, though it must be very difficult to make these matters plain to a person who lacks a mind for figures. In only two respects does one feel a deficiency in the book. We should have liked something about the voice as a musical instrument to supplement a good chapter on hearing, and some account of the working of instruments in which the sounds are electrically produced. But perhaps the author, as an organist, joins the ranks of those who deplore such imitations, though it is time for the Hammond electric organ to get a paragraph. In short, a book which should appeal to all whose interests are both musical and scientific

E. G. R.

Personality Survives Death, by LADY BARRETT. With a foreword by Canon R. J. CAMPBELL. Pp. xlvi + 204. (Longmans Green and Co.) Price 7*s*. 6*d*. net.

Coming as it does from the pen of one so established in the scientific world, this book cannot fail to arouse interest in those quarters. The writer styles herself editor of the messages contained therein, which purport to be communications from her late husband, Sir William Barrett, F.R.S. As founder, in 1881, of the Society for Psychical Research, he was wont to state that his interest in psychical research arose out of his experience as a physicist. There seems to be nothing in this small volume in disaccord with that statement. It is apparent that the matter contained in the messages owes its origin to a scientifically trained intellect which is not likely to be that of the medium. The initial difficulty experienced by most enquirers—namely, the reason for so many apparently futile communications—is dealt with more satisfactorily than in previous publications on the subject. And there is scarcely a sentimental word. Certain of the tests recorded leave the reader with but two alternatives—either to accept the message as genuine or to doubt the veracity of the recorder.

An interesting study for those of sceptical mind.

L. P. T.